George T. Austin

SHREVE'S CHEMICAL PROCESS INDUSTRIES

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MINISTRY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF

TECHNICAL AND VOCATIONAL EDUCATION

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CHEMICAL TECHNOLOGY III

B.E

Chemical Engineering

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Chapter 1

Fragrances, Flavors, and Food Additives

THE PERFUME[1] INDUSTRY

The manufacture of perfume, cologne, and toilet water, collectively known as the fragrances has undergone drastic changes in the past quarter century, prior to which perfumers were usually trained through apprenticeships in laboratories until, working with traditional materials in well-defined patterns, they achieved skill in mixing and blending. Only occasionally was a new and original odor developed, such as Old Spice, which immediately won spontaneous and favorable response from consumers. Not many people realize how complex the creation of an acceptable fragrance has become; it requires professional knowledge, skill, and experience, coupled with specialization in synthetic chemistry's technical problems, followed by consumer panel testing. This change has resulted from a number of factors, for example: (1) increase in the number of available raw-material ingredients, both natural and synthetic; (2) a variety of new types of products requiring fragrances; (3) innovations in packaging, especially aerosol sprays, virtually nonexistent before 1950, and other new forms of dispensing such as perfume powders, cream sachets, gels, lotions, and sticks; (4) broadened channels and methods of distribution, including door-to-door selling; and (5) phenomenal growth in men's toiletries. These numerous recent developments are in contrast to the two main changes which took place earlier, the introduction of synthetics and improved methods of obtaining true oils.

Perfume takes its name from the Latin word *perfumare* (to fill with smoke), since in its original form it was incense burned in Egyptian temples. Early incenses were merely mixtures of finely ground spices held together by myrrh or storax. The next advance was the discovery that, if certain spices and flowers were steeped in fat or oil, the fat or oil would retain a portion of the odoriferous principle. Thus were manufactured the ointments and fragrant unguents of Biblical fame. Avicenna, the Arabian physician, discovered steam distillation of volatile oils. During his search for medical potions, he found that flowers boiled in an alembic with water gave up some of their essence to the distillate. The returning Crusaders brought to Europe all the art and skill of the orient in perfumery, as well as information relating to sources of gums, oils, and spices. René, perfumer to Catherine de' Medici, invented many new confections to delight the queenly nose and, in his spare time, was one of the cleverest and deadliest of the famous de' Medici poisoners. Many of the finest perfumes are imported from France. Classical colognes are at least 200 years old, having originated in

[1]ECT, 3d ed., vol. 16, 1982, p. 947.

Cologne, Germany; they were probably the first imports into this country. It was not until the 1950s that U.S. industry discovered that the sale of perfume odors in an alcohol-diluted form was profitable.

USES AND ECONOMICS. Fragrance shipments were $1800 million in 1981, and this was a large increase from the $320 million in 1974. The popularity of men's fragrances has, no doubt, contributed greatly to the increase.

Fragrances make a major contribution to the cosmetic industry, second only to the amount used in soaps and detergents. Fragrances are used industrially in masking, neutralizing, and altering the odor of various products, as well as in creating a distinctive aroma for normally odorless objects. Cashmere shawls manufactured in Scotland are given the Hindu touch by a trace of patchouli oil applied to them. Aromatics, sometimes referred to as *reodorants*, are added to fabric sizing to disguise the glue or casein smell, leaving the product with a fine fresh odor. Leather goods and papers are scented delicately to eliminate the raw-material smell. The odor of kerosene in fly sprays is masked; artificial cedarwood is made by coating other woods with cedar oil reclaimed in pencil manufacturing. Canneries, rendering plants, municipal refuse plants, and food processing systems are other areas where reodorants are used. Paint odor during drying is masked by essential oils and fixatives introduced in small quantities in the bulk product. Odors are used successfully to increase customer appeal, though they are not essential to the performance of the products to which they are added.[2] A minute amount of bornyl acetate evaporated in an air-conditioning system imparts an outdoor tang to the air.

Constituents

A perfume may be defined as any mixture of pleasantly odorous substances incorporated in a suitable vehicle. Formerly, practically all the products used in perfumery were of natural origin. Even when humans first started synthesizing materials for use in this field, they endeavored to duplicate the finest in nature. There has been a marked tendency in recent years, however, to market perfumes which have no exact counterpart in the floral kingdom but which have received wide acceptance. The finest modern perfumes are neither wholly synthetic nor completely natural. The best product of the art is a judicious blend of the two in order to enhance the natural perfume, to reduce the price, and to introduce fragrances into the enchanting gamut at present available. A product made solely of synthetics tends to be coarse and unnatural because of the absence of impurities in minute amounts which finish and round out the bouquet of natural odors; however, such an eventual development is predicted. The chemist has also succeeded in creating essences of flowers which yield no natural essence or whose essence is too expensive or too fugitive to make its extraction profitable. Lily of the valley, lilac, and violet are examples. The constituents of perfumes are: the vehicle or solvent, the fixative, and the odoriferous elements.

VEHICLES. The modern solvent for blending and holding perfume materials is highly refined ethyl alcohol mixed with more or less water according to the solubilities of the oils employed. This solvent, with its volatile nature, helps to project the scent it carries, is fairly inert to the

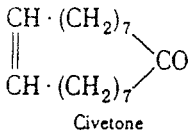
[2]Mitchell et al., "Importance of Odor as a Nonfunctional Component," Odor Symposium, New York Academy of Sciences, November 7–9, 1963.

solutes, and is not too irritating to the human skin. The slight natural odor of the alcohol is removed by deodorizing, or "prefixation," of the alcohol. This is accomplished by adding a small amount of gum benzoin or other resinous fixatives to the alcohol and allowing it to mature for a week or two. The result is an almost odorless alcohol, the natural rawness having been neutralized by the resins.

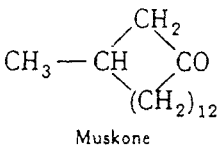
FIXATIVES. In an ordinary solution of perfume substances in alcohol, the more volatile materials evaporate first, and the odor of the perfume consists of a series of impressions rather than the desired ensemble. To obviate this difficulty, a fixative is added. Fixatives may be defined as substances of lower volatility than the perfume oils, which retard and even up the rate of evaporation of the various odorous constituents. The types of fixative considered are animal secretions, resinous products, essential oils, and synthetic chemicals. Any of these fixatives may or may not contribute to the odor of the finished product but, if they do, they must blend with and complement the main fragrance.

Animal Fixatives. Of all animal products, *castor*, or *castoreum*, a brownish orange exudate of the perineal glands of the beaver, is employed in the greatest quantity. Among the odoriferous components of the volatile oil of castor are benzyl alcohol, acetophenone, *l*-borneol, and castorin (a volatile resinous component of unknown structure).

Civet is the soft, fatty secretion of the perineal glands of civet cats, which are indigenous to many countries, and was developed in Ethiopia. The secretions are collected about every 4 days by spooning and are packed for export in hollow horns. The crude civet is disagreeable in odor because of the skatole present. On dilution and aging, however, the skatole odor disappears, and the sweet and somewhat floral odor of civetone, a cyclic ketone, appears.



Civetone



Muskone

Musk is the dried secretion of the preputial glands of the male musk deer, found in the Himalayas. The odor is due to a cyclic ketone called *muskone*, which is present to the extent of from ½ to 2%. Musk, the most useful of the animal fixatives, imparts body and smoothness to a perfume composition even when diluted so that its own odor is completely effaced. Musk is used for its own sake in heavy oriental perfumes.

Ambergris is the least used, but probably best known, of the animal fixatives. It is a calculus, or secretion, developed by certain whales. Ambergris is obtained by cutting open the captured whale, or it is obtained from whales stranded on a beach. It is waxy in consistency, softening at about 60°C, and may be white, yellow, brown, black, or variegated like marble. It is composed of 80 to 85% ambrein (triterpenic tricyclic alcohol), resembling cholesterol and acting merely as a binder, and 12 to 15% ambergris oil, which is the active ingredient. It is employed as a tincture, which must be matured before it is used. The odor of the tincture is decidedly musty and has great fixative powers.

Musc zibata is the newest animal fixative, derived from glands of the Louisiana muskrat. It was only during World War II that musc zibata was commercialized. About 90% of the unsaponifiable material in muskrat glands consists of large, odorless cyclic alcohols, which are converted to ketones, increasing the characteristic musk odor nearly 50 times. It is a replacement for, or an addition to, Asiatic musk.

Resinous Fixatives. Resinous fixatives are normal or pathological exudates from certain plants, which are more important historically than commercially. These are hard resins, e.g., benzoin and gums; softer resins, e.g., myrrh and labdanum; balsams, moderately soft, e.g., Peru balsam, tolu balsam, copiaba, and storax; oleoresins, oily materials, e.g., terpenes; extracts from resins, less viscous, e.g., ambrein. All these substances, when being prepared for perfume compounding, are dissolved and aged by methods passed down by word of mouth. If solution is brought about in the cold, the mixture is called a *tincture*. If heat is required to give solution, the mixture is an *infusion*. Alcohol is the solvent, sometimes aided by benzyl benzoate or diethyl phthalate. The most important of the soft gums is *labdanum*. The leaves of a plant growing in the Mediterranean area exude this sticky substance. An extract from this gum has an odor suggestive of ambergris and is marked as *ambrein*, having extremely good fixative value. Of the harder plant resins used in perfumes, *benzoin* is the most important. The history of chemistry was influenced by this substance. The early source of benzoin was Java, where it was called *luban jawi*. Through various contractions and linguistic modifications, it became "banjawi," "benjui," "benzoi," "benzoin," and "benjamin." In early organic chemical history an acid isolated from this gum became known as *benzoic acid*, from which compound the names of all benzo compounds of today are derived.

Essential-Oil Fixatives. A few essential oils are used for their fixative properties as well as their odor. The more important of these are clary sage, vetiver, patchouli, orris, and sandalwood. These oils have boiling points higher than normal (285 to 290°C).

Synthetic Fixatives. Certain high-boiling, comparatively odorless esters are used as fixatives to replace some imported animal fixatives. Among them are glyceryl diacetate (259°C), ethyl phthalate (295°C), and benzyl benzoate (323°C). Other synthetics are used as fixatives, although they have a definite odor of their own that contributes to the ensemble in which they are used. A few of these are

Amyl benzoate	Musk ketone	Heliotropin
Phenethyl phenylacetate	Musk ambrette	Hydroxycitronellal
Cinnamic alcohol esters	Benzophenone	Indole
Cinnamic acid esters	Vanillin	Skatole
Acetophenone	Coumarin	

ODOROUS SUBSTANCES. Most odorous substances used in perfumery come under three headings: (1) essential oils, (2) isolates, and (3) synthetic or semisynthetic chemicals.

Essential Oils.[3] Essential oils may be defined as volatile, odoriferous oils of vegetable origin (Table 1.1). A distinction should be made, however, between natural flower oils obtained by enfleurage or solvent extraction and essential oils recovered by distillation. Distilled oils may lack some component which is not volatile enough or which is lost during distillation. Two notable examples of this are rose oil, in which phenylethyl alcohol is lost to the watery portion of the distillate, and orange flower oil, in which the distilled oil contains

[3]"Essential" does not mean "most necessary" but rather the concentrated characteristic or quintessence of a natural flavor or fragrance raw material; *International Standardization of Essential Oils*, Committee ISO/TC54 publishes standards. See *Cosmet. Perfum.* 90 (2) 86 (1975).

Table 1.1 Important Essential Oils

Name of Oil	Important Geographical Sources	Method of Production	Part of Plant Used	Chief Constituents
Almond, bitter	California, Morocco	Steam	Kernels	Benzaldehyde 96–98%, HCN 2–4%
Bay	West Indies	Steam	Leaves	Eugenol 50%
Bergamot	Southern Italy	Expression	Peel	Linalyl acetate 40%, linalool 6%
Caraway	Northern Europe, Holland	Steam	Seed	Carvone 55%, *d*-limonene
Cassia (Chinese cinnamon)	China	Steam	Leaves and twigs	Cinnamic aldehyde 70%
Cedarwood	North America	Steam	Red core wood	Cedrene, cedral
Cinnamon	Ceylon	Steam	Bark	Cinnamic aldehyde, eugenol
Citronella, Java	Java, Ceylon	Steam	Grass	Geraniol 65%, citronellal
Clove	Zanzibar, Madagascar, Indonesia	Steam	Buds (cloves)	Eugenol 85–95%
Coriander	Central Europe, Russia	Steam	Fruit	Linalool, pinene
Eucalyptus	California, Australia	Steam	Leaves	Cineole (eucalyptole) 70–80%
Geranium	Mediterranean countries	Steam	Leaves	Geraniol esters 30%, citronellol
Jasmine	France, Egypt, Italy	Cold pomade	Flowers	Benzyl acetate, linalool, and esters
Lavender	Mediterranean area	Distillation	Flowers	Linalool
Lemon	California, Sicily	Expression	Peel	*d*-Limonene 90%, citral 3.5–5%
Orange, sweet	Florida, California, Mediterranean area	Expression, distillation	Peel	*d*-Limonene 90%
Peppermint	Michigan, Indiana, etc.	Steam	Leaves and tops	Menthol 45–90% and esters
Rose	Bulgaria, Turkey	Steam, solvent, enfleurage	Flowers	Geraniol and citronellol 75%
Sandalwood	India, East Indies	Steam	Wood	Santalol 90%, esters 3%
Spearmint	Michigan, Indiana	Steam	Leaves	Carvone 50–60%
Tuberose	France	Enfleurage, solvent extraction	Flowers	Tuberose oil
Wintergreen (gaultheria)	Eastern United States	Steam	Leaves	Methyl salicylate 99%
Ylang-ylang	Madagascar, Philippines	Steam, solvent extraction	Flowers	Esters, alcohols

but a very small proportion of methyl anthranilate, whereas the extracted flower oil may contain as much as one-sixth of this constituent

Essential oils are, in the main, insoluble in water and soluble in organic solvents, although enough of the oil may dissolve in water to give an intense odor to the solution, as in the case of rose water and orange flower water. These oils are volatile enough to distill unchanged in most instances, and are also volatile with steam. They vary from colorless to yellow or brown in color. An essential oil is usually a mixture of compounds, although oil of wintergreen is almost pure methyl salicylate. The refractive indexes of the oils are high, averaging about 1.5. The oils show a wide range of optical activity, rotating in both directions

The compounds occurring in essential oils may be classified as follows

1. *Esters.* Mainly of benzoic, acetic, salicylic, and cinnamic acids
2. *Alcohols.* Linalool, geraniol, citronellol, terpinol, menthol, borneol
3. *Aldehydes.* Citral, citronellol, benzaldehyde, cinnamaldehyde, cuminic aldehyde vanillin
4. *Acids.* Benzoic, cinnamic, myristic, isovaleric in the free state
5. *Phenols.* Eugenol, thymol, carvacrol
6. *Ketones.* Carvone, menthone, pulegone, irone, fenchone, thujone, camphor methyl nonyl ketone, methyl heptenone
7. *Esters.* Cineole, internal ether (eucalyptole), anethole, safrole
8. *Lactones.* Coumarin
9. *Terpenes.* Camphene, pinene, limonene, phellandrene, cedrene
10. *Hydrocarbons.* Cymene, styrene (phenylethylene

In living plants essential oils are probably connected with metabolism, fertilization, or protection from enemies. Any or all parts of the plant may contain oil. Essential oils are found in buds, flowers, leaves, bark, stems, fruits, seeds, wood, roots, and rhizomes and in some trees in oleoresinous exudates.

Volatile oils may be recovered from plants by a variety of methods[4]: (1) expression, (2) distillation, (3) extraction with volatile solvents, (4) enfleurage, and (5) maceration. The majority of oils are obtained by distillation, usually with steam, but certain oils are adversely affected by the temperature. Distilled citrus oils are of inferior quality; therefore they are derived by expression. For certain flowers which yield no oil upon distillation or else deteriorated oil, the last three methods are used. However, extraction with volatile solvents, a comparatively recent process, has superseded maceration (extraction with hot fat) for all practical purposes and is replacing enfleurage. Solvent extraction is the most technically advanced process and yields truly representative odors, but is more expensive than distillation

Distillation, usually with steam. Flowers and grasses are normally charged into the still without preparation. Leaves and succulent roots and twigs are cut into small pieces. Dried materials are powdered. Woods and tough roots are sawed into small pieces or mechanically chipped. Seeds and nuts are fed through crushing rolls spaced so as to crack them. Berries are charged in the natural state, since the heat of distillation soon develops enough pressure to burst their integument. The stills employed in factories are of copper, tin-lined copper, or stainless steel and of about 2300 L capacity. They are provided with condensers of various sorts, tubular ones being the more efficient, and with a separator for dividing the oily layer from the aqueous one. Although removable baskets for holding the material to be distilled are used, the better procedure seems to be to construct the still with a perforated false plate lying just above the bottom. Underneath this false bottom are steam coils, both closed and

[4]Dorland and Rogers, *The Fragrance and Flavor Industry*, Dorland, Mendham, N.J., 1977.

perforated. In operating these stills, the charge is heated by steam in both the closed and the open pipes, thus effecting economical steam distillation. The aqueous layer in the condensate frequently carries, in solution, valuable constituents, as in the case of rose and orange flower oil, and is consequently pumped back into the still to supply some of the necessary water. Steam distillation usually is carried out at atmospheric pressure. If the constituents of the oil are subject to hydrolysis, the process is carried out in a vacuum. Much distillation for essential oils is done at the harvest site in extremely crude stills. These stills are converted oil drums or copper pots equipped with pipe condensers running through water tubs. The material and water are charged into the still, and a direct fire of dried material exhausted in previous distillations is built underneath. The efficiency is low, and the oil is contaminated with pyrolysis products, such as acrolein, trimethylamine, and creosotelike substances. The crude oils obtained from the stills are sometimes further treated before use by vacuum-rectification, by fractional freezing (e.g., menthol from Japanese peppermint oil), by washing with potassium hydroxide to remove free acids and phenolic compounds, by removal of wanted or unwanted aldehydes and ketones through formation of the bisulfite addition compounds, or by formation of specific insoluble products, as in the reaction of calcium chloride with geraniol.

Expression by machine can yield an oil almost identical to the hand-pressed product, and is the method used commercially. Of the hand-pressed processes, the *sponge* process is the most important, since it produces the highest-quality oil. Here the fruit is halved, and the peel trimmed and soaked in water for several hours. Each peel is pressed against a sponge, and the oil is ejected into the sponge, which is periodically squeezed dry. One person can prepare only 680 g of lemon oil a day by this method, but it is still practiced, especially in Sicily.

Enfleurage. The enfleurage process is a cold-fat extraction process used on a few types of delicate flowers (jasmine, tuberose, violet, etc.) which yield no direct oil at all on distillation. In the case of jasmine and tuberose, the picked flowers continue to produce perfume as long as they are alive (about 24 h). The fat, or base, consists of a highly purified mixture of 1 part tallow to 2 parts lard, with 0.6% benzoin added as a preservative. This method is no longer used commercially.

Extraction with volatile solvents. The most important factor in the success of this practice is the selection of the solvent. The solvent must (1) be selective, i.e., quickly and completely dissolve the odoriferous components, but have only a minimum of inert matter, (2) have a low boiling point, (3) be chemically inert to the oil, (4) evaporate completely without leaving any odorous residue, and (5) be low-priced and, if possible, nonflammable. Many solvents have been used, but highly purified petroleum ether is the most successful, with benzene ranking next. The former is specially prepared by repeated rectification and has a boiling point no higher than 75°C. When benzene is employed, it is specially purified by repeated crystallization. The *extraction equipment* is complicated and relatively expensive and consists of stills for fractionating the solvent, batteries for extracting the flowers, and stills for concentrating the flower-oil solutions. The two types of extractors employed are the stationary and rotary types.

In the rotary process the oil is extracted on the *countercurrent principle.* The 1325-L steam-jacketed drums revolve around a horizontal axis and are divided into compartments by perforated plates at right angles to the axis. About 135 kg of flowers is charged into the first drum, along with 575 L of petroleum ether which has already come through the other two drums. The drum and its contents are rotated for an hour cold and for an additional half hour with steam in the jacket. The saturated solvent is pumped to the recovery still, and the flowers in the drum are treated twice more, the second time with once-used solvent and the last time with fresh solvent from the recovery still. The exhausted flowers are blown with

steam to recover the adhering solvent. About 90 percent of the solvent is boiled off at atmospheric pressure, and the rest is removed under vacuum. After the solvent is removed in either process, the semisolid residue contains the essential oil, along with a quantity of waxes, resins, and coloring material from the blossoms. This pasty mass is known as *concrete*. In turn it is treated with cold alcohol in which most of the wax and resin are insoluble. The small amount of unwanted material that dissolves is removed by cooling the solution to −20°C and filtering it. The resulting liquid contains the essential oil and some of the ether-soluble color of the flower and is known as an *extract*. When the alcohol has been removed, an *absolute* remains.

In some oils there is a large quantity of *terpenes*. This is especially true in the case of lemon and orange oils, which have as much as 90% *d*-limonene in their normal composition. Not only are terpenes and sesquiterpenes of exceedingly little value to the strength and character of the oils, but they also oxidize and polymerize rapidly on standing to form compounds of a strong turpentine-like flavor. Furthermore, terpenes are insoluble in the lower strengths of alcohol used as a solvent and make cloudy solutions which are cleared up only with difficulty. Hence it is desirable to remove terpenes and sesquiterpenes from many oils. Such an oil, orange, for example, is 40 times as strong as the original and makes a clear solution in dilute alcohol. The oil has now very little tendency to rancidify, although it has not quite the freshness of the original. These treated oils are labeled "tsf" (terpene- and sesquiterpene-free). Because each oil has a different composition, *deterpenation* requires a special process. Two methods are involved, either the removal of the terpenes, sesquiterpenes, and paraffins by fractional distillation under vacuum, or extraction of the more soluble oxygenated compounds (principal odor carriers) with dilute alcohol or other solvents.

Because of the complex nature and the high price commanded by so many essential oils, a great deal of adulteration, or sophistication, is practiced. These additions were formerly extremely hard to detect in most cases since, whenever possible, a mixture of adulterants is used that does not change the physical constants of the oil. Common agents used are alcohol, cedar oil, turpentine, terpenes, sesquiterpenes, and low specific gravity liquid petroleums. The advent of so many esters of glycol and glycerol on the market increased the difficulty of detection, since these compounds are colorless and practically odorless and in the right combination can be made to simulate almost any specific gravity and refractive index specifications set up for the oil they are intended to adulterate. The modern use of gas chromatography (GC) has made it possible to detect easily even small amounts of adulterants. Rose oil may be sophisticated with geraniol or a mixture of geraniol and citronellol; wintergreen and sweet birch oil are mixed with large amounts of synthetic methyl salicylate; and lemon oil is often "stretched" considerably with citral from lemon grass oil.

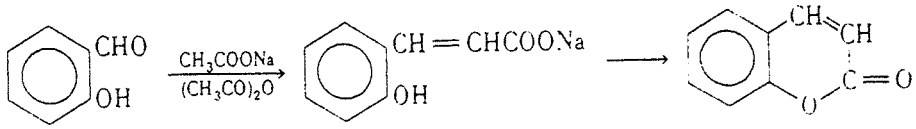
Isolates. Isolates are pure chemical compounds whose source is an essential oil or other natural perfume material. Notable examples are eugenol from clove oil, pinene from turpentine, anethole from anise oil, and linalool from linaloa oil (bois de rose).

SYNTHETICS AND SEMISYNTHETICS USED IN PERFUMES AND FLAVORS.[5] More and more important constituents of perfumes and flavors are being made by the usual chemical synthetic procedures. Compositions containing predominantly inexpensive synthetics now account for more than 50 percent of the fragrances used in perfumes. Some constituents are chemically synthesized from an isolate or other natural starting materials and are classed as

[5]Poucher, *Perfumes, Cosmetics and Soaps*, vol. II, Wiley, New York, 1974; Clark and Grande, Study of Odor Variation with Structural Change, *Cosmet. Perfum.* 90 (6) 58 (1975); Chemicals from Trees, *CHEMTECH*, 5 236 (1975).

semisynthetics. Examples are vanillin, prepared from eugenol from clove oil; ionone, from citral from lemon grass oil; and terpineols, from turpentine and pine oil. Some of the significant synthetics are discussed below. The examples presented are grouped under the most important chemical conversion.

Condensation Processes[6] *(Fig. 1.1).* *Coumarin* occurs in tonka beans and 65 other plants, but the economical source is the synthetic. It is employed as a fixative and enhancing agent for essential oils and tobacco products, and as a masking agent for disagreeable odors in industrial products. The synthetic product may be prepared[7] in a number of different ways. One method utilizes the Perkin reaction:



Salicylaldehyde, acetic anhydride, and sodium acetate are refluxed at 135 to 155°C. The reaction mixture is cooled and washed. The coumarin is recovered by solvent extraction or distillation. Other important methods of coumarin preparation utilize *o*-cresol as the starting

[6]Process-Studded Plant: Key to Fragrance, *Chem. Eng.* 65 (4) 112 (1958).

[7]ECT, 3d ed., vol. 7, 1979, p. 196.

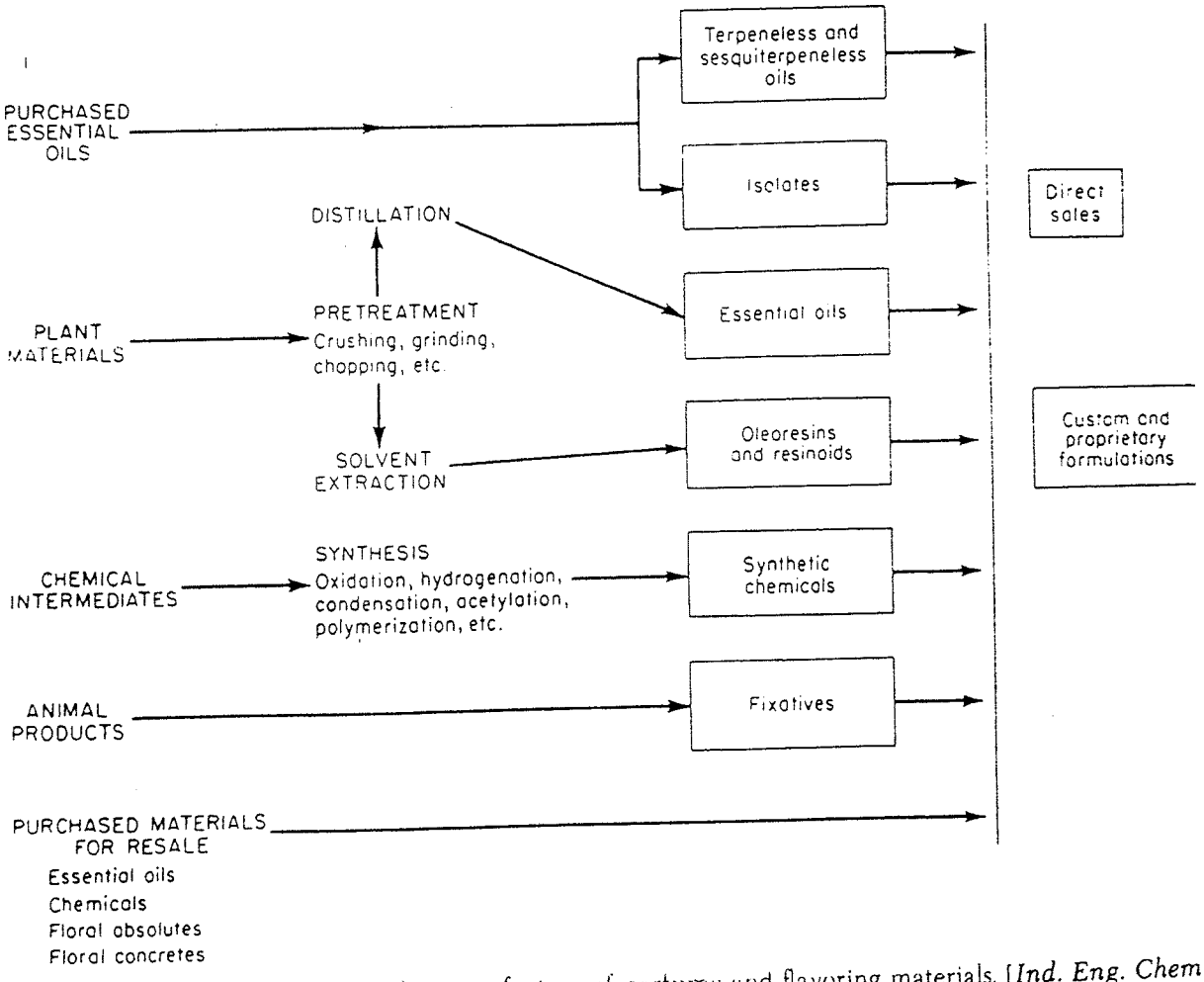


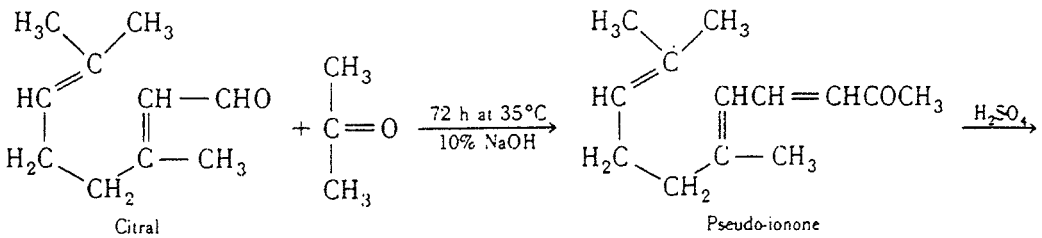
Fig. 1.1. Outline flowchart for the manufacture of perfume and flavoring materials. [*Ind. Eng. Chem* 53 *(6) 422 (1961); courtesy of Fritzsche Bros.*]

material, or the Hassmann-Reimer synthesis, where coumarin-3-carboxylic acid is produced as an intermediate. Over 450,000 kg is produced per year.

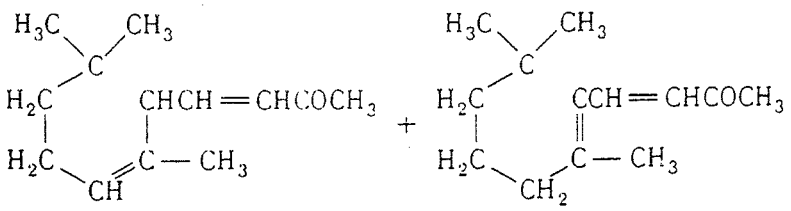
Diphenyl oxide, or *ether*, is largely used in the soap and perfume industries because of its great stability and strong geranium odor. Diphenyl oxide is obtained as a by-product in the manufacture of phenol from chlorobenzene and caustic soda.

$$2C_6H_5OH \rightleftharpoons C_6H_5OC_6H_5 + H_2O$$

Ionone and its homologs possess the so-called violet type of odor, thus constituting the base of violet perfumes. These compounds, however, are indispensable to fine perfumes, and there are but few which do not contain at least a small percentage of ionones. Annually, about 225,000 kg of ionones is produced. Because of the high price of the natural oil of violet, this was one of the first essential oils synthesized, although it has since been found in certain obscure plants. The olfactory properties of ionone are due to the presence of *dl*-α-ionone and β-ionone. Their manufacture involves two steps: First, the pseudo-ionone is prepared by the condensation of citral obtained from lemon grass oil. This is followed by an acid ring closure, and the commercial ionone is purified by distillation. Commercial ionones are generally mixtures with one form predominating, although separations are sometimes made through bisulfite compounds.



Citral — Pseudo-ionone



α-Ionone — β-Ionone

Cinnamic aldehyde has a cinnamon odor. As it oxidizes in air to cinnamic acid, it should be protected from oxidation. Although this aldehyde is obtained from Chinese cassia oils, it is synthesized by action of alkali upon a mixture of benzaldehyde and acetaldehyde (Fig. 27.2). The production is about 365,000 kg per year.

$$C_6H_5CHO + CH_3CHO \xrightarrow{NaOH} C_6H_5CH{:}CHCHO + H_2O$$

This and most other products for fragrances must be purified, for example, by vacuum fractionation (Fig. 27.3).

Esterification Processes. *Benzyl benzoate* has a faint aromatic odor, boils at 323 to 324°C, and is a fixative and a flavoring material. It occurs naturally in balsams (Peru, Tolú) but is prepared commercially by the esterification of benzoic acid with benzyl alcohol or by the Cannizzaro reaction with benzaldehyde.

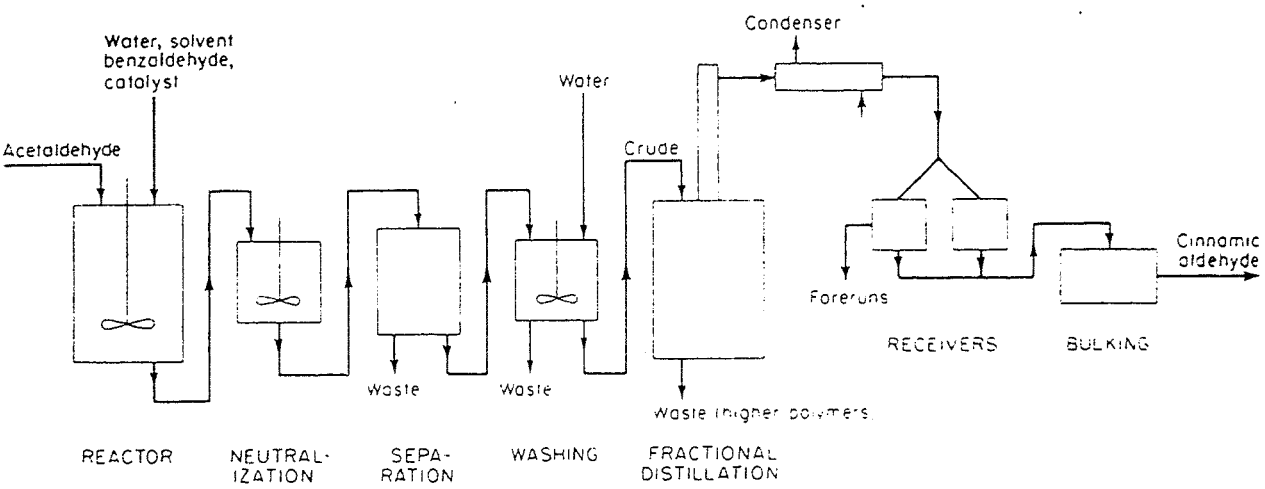


Fig. 1.2. Flowchart for cinnamic aldehyde production by aldol condensation. *(Fritzsche Bros., Inc.)*

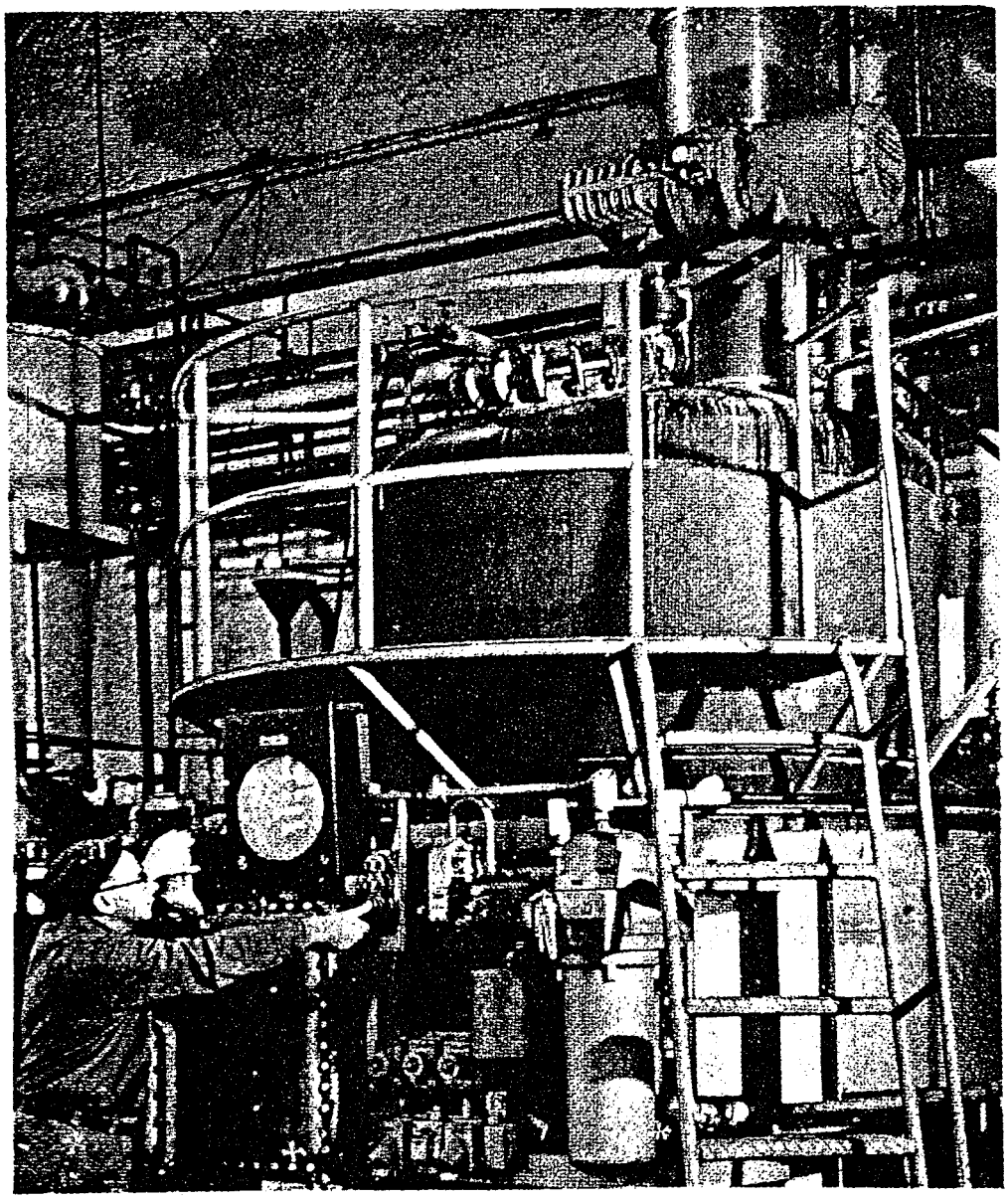


Fig. 1.3. High-temperature vacuum fractionating equipment. *(Fritzsche Bros., Inc.)*

Two esters of *salicylic acid* (*o*-hydroxy benzoic acid) are very important commercially in the perfume and flavoring industries. About 160,000 kg of *amyl salicylate* is used annually in a variety of perfumes, because of its lasting quality and low price. About 1.8×10^6 kg of *methyl salicylate* (synthetic wintergreen oil) is consumed annually as a flavoring ingredient. These esters are prepared as follows: Carbon dioxide and sodium phenate are reacted under pressure to obtain the salt of phenylcarbonic acid. This salt is isomerized to sodium salicylate by heating to 120 to 140°C. The esters are made from the acid and the proper alcohol.

Benzyl acetate ($C_6H_5CH_2OCOCH_3$) is another widely used ester because of its low cost and floral odor. About 450,000 kg is sold annually for soap and industrial perfumes. It is prepared by esterification of benzyl alcohol, by heating with either an excess of acetic anhydride or acetic acid with mineral acids. The product is purified by treatment with boric acid and distilled, giving a purity of over 98%. Large amounts of *benzyl alcohol* are employed in pharmaceuticals, lacquers, etc. (about 1.8×10^6 kg per year). This alcohol has a much weaker odor than its esters. It is made by hydrolyzing benzyl chloride.

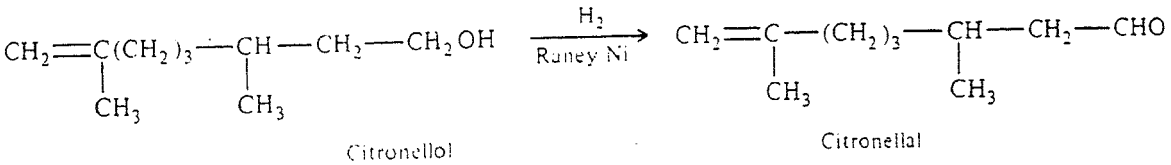
Grignard Processes. *Phenylethyl alcohol* has a roselike odor and occurs in the volatile oils of rose, orange flowers, and others. It is an oily liquid and is much used in perfume formulation, more than 450,000 kg being sold annually. Phenylethyl alcohol can be made by a number of procedures; the Grignard reaction is used generally:

$$C_6H_5Br \xrightarrow{Mg\ (ether)} C_6H_5MgBr \xrightarrow{CH_2-CH_2\ \diagdown O\ \diagup} C_6H_5 \cdot CH_2CH_2OMgBr \xrightarrow{acid} C_6H_5 \cdot CH_2CH_2OH$$

However, the Friedel-Crafts reaction is outlined in the flowchart in Fig. 1.4 and follows the reaction

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\substack{\text{Ethylene}\\ \text{oxide}}}{(CH_2)_2O} \xrightarrow{AlCl_3} C_6H_5 \cdot CH_2CH_2OH$$

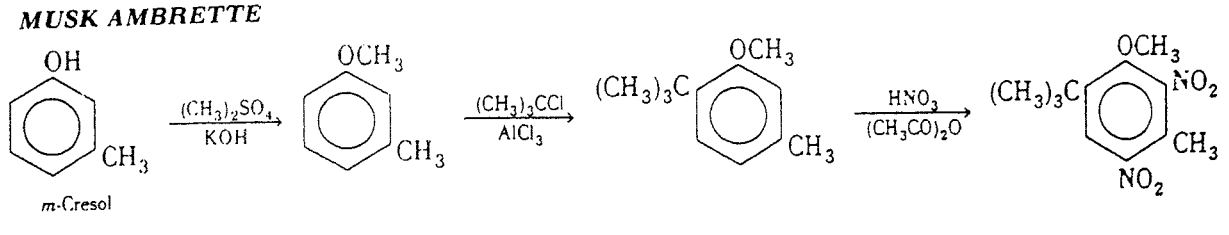
Hydrogenation. See Fig. 1.5 for citronellal from citronellol by Raney nickel hydrogenation at 1375 kPa.



Citronellol — Citronellal

Nitration Processes. *Artificial musks* comprise a number of products not identical with the natural musk, which derives its odor from macrocyclic compounds. Nitro musks are practical and economical substitutes for this expensive natural fixative, and more than 90,000 kg of musk xylene alone is manufactured annually. The reactions for the three important commercial artificial musks are

MUSK AMBRETTE



m-Cresol

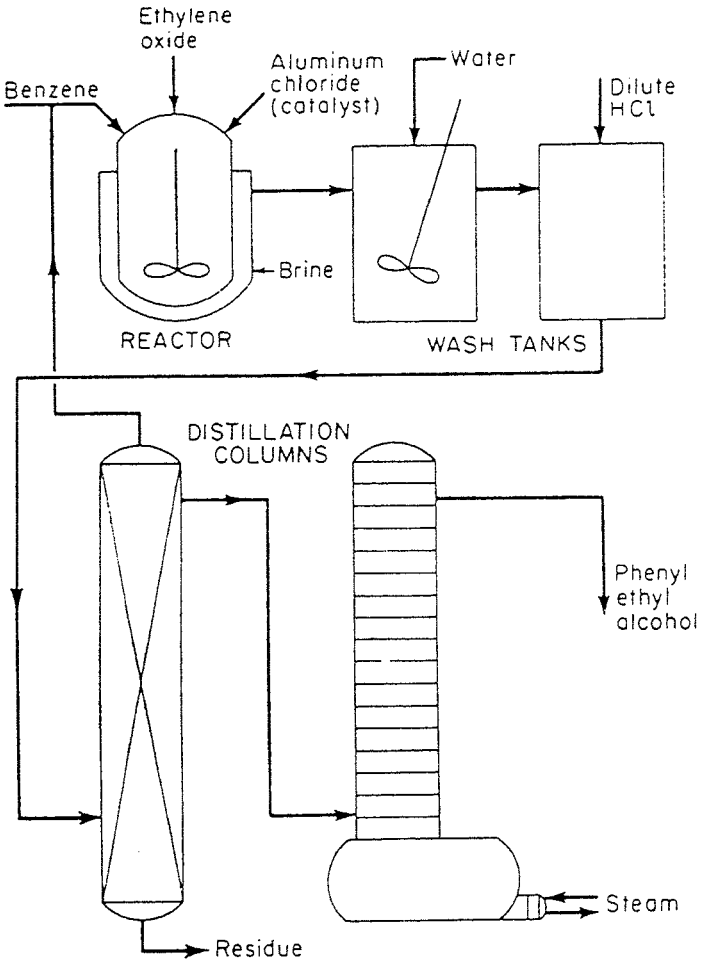
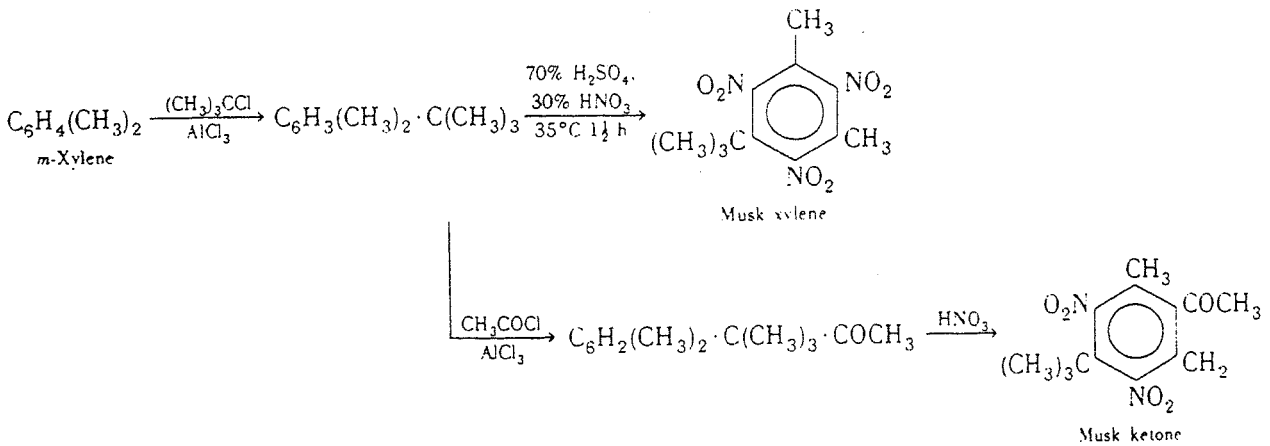


Fig. 1.4. Phenylethyl alcohol formed by the Friedel-Crafts reaction. [*Chem. Eng.* 65 *(4) 113 (1958); courtesy of Van Amerigen Haebler.*]

MUSK XYLENE AND MUSK KETONE



Oxidation Processes. *Vanillin* is one of the most widely used flavors, more than 680,000 kg/year being manufactured. It is used as a flavor in perfumery and for deodorizing manufactured goods. Many processes have been employed in its manufacture, such as the following:

1. From eugenol from oil of cloves, through isoeugenol, followed by oxidation to vanillin, using nitrobenzene as the oxidizing agent:

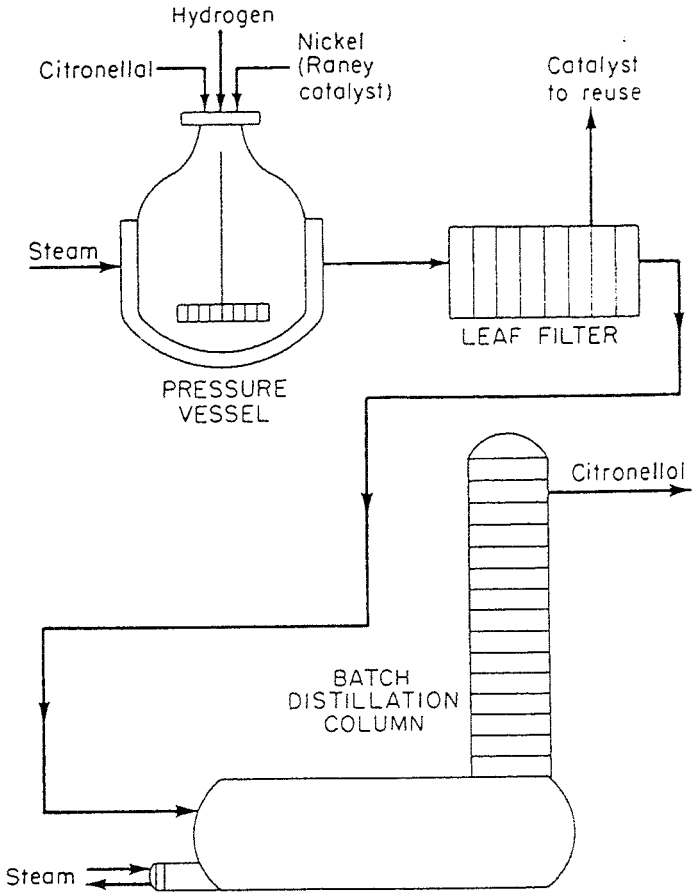
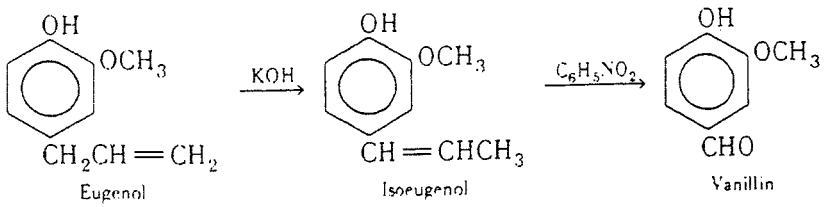


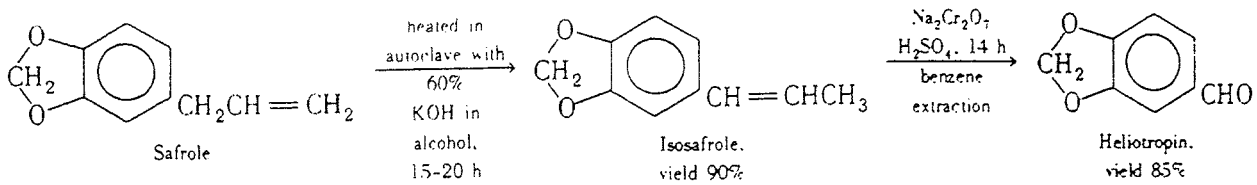
Fig. 1.5. Hydrogenation under pressure of 1380 kPa to convert citronellal to citronellol. [*Chem. Eng.* 65 *(4) (1958): courtesy of Van Amerigen Haebler.*]



2. From lignin[8] through an alkaline pressure cook at 900 to 1400 kPa for ½ to 1 h. The vanillin is purified through the sodium bisulfite compound and extraction with benzene or isopropanol (Fig. 1.6). Most of the vanillin on the market is made this way.

3. From phenol[9] or *o*-chloronitrobenzene through guaiacol, following the usual synthetic procedure.

Heliotropin, or *piperonal*, has a pleasant aromatic odor resembling heliotrope. It is produced from safrole by the following reactions:



[8]Craig *et al.*, U.S. Patent 3,054,659 (1962); ECT, 3d ed., vol. 14, 1981, p. 306.

[9]Schwyzer, Die Fabrikation pharmazeutischer und chemischtechnischer Produkte, Springer, Berlin, 1931, pp. 205–209, 279–288.

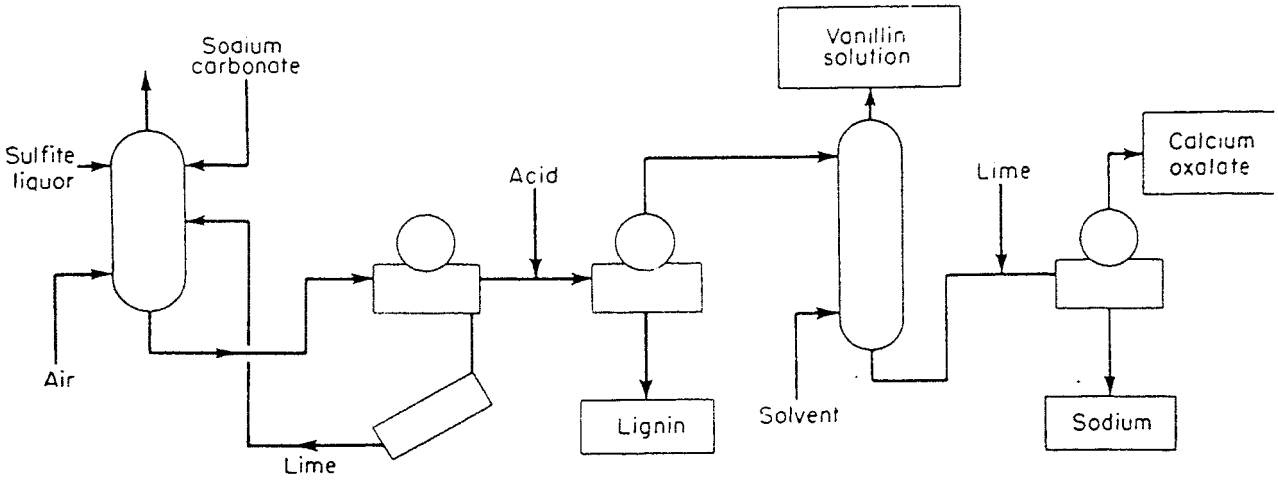
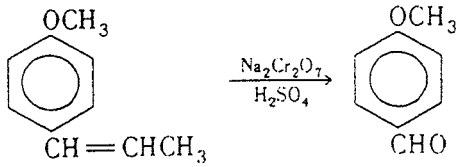


Fig. 1.6. Vanillin from lignin. [*Chem. Week* 89 *(37) 103 (1961).*]

Anisaldehyde is a colorless oily liquid with an agreeable odor resembling coumarin, which is developed only after dilution and in mixtures. It is made by the oxidation of anethole (the chief constituent of anise, star anise, and fennel oils). Anethole has been obtained recently in this country at very low cost from higher-boiling fractions of pine oil.



Benzaldehyde is used as a flavoring agent, as an ingredient in pharmaceuticals, and as an intermediate in chemical syntheses. Commercially, it is produced by several methods and in two grades, technical and refined. The technical grade is largely used as an intermediate in the synthesis of other chemicals, such as benzyl benzoate, cinnamic aldehyde, and dyes. Most of the technical grade is made by direct vapor-phase oxidation of toluene, although some is made by chlorinating toluene to benzal chloride, followed by alkaline or acid hydrolysis. For perfume and flavoring use, the refined, chlorine-free grade is required, which is economically produced by the direct vapor-phase oxidation of toluene. This oxidation is sometimes carried out in the liquid phase.

VAPOR PHASE

$$C_6H_5CH_3 \xrightarrow[500°C]{\text{air, catalyst}} C_6H_5CHO + H_2O \qquad \Delta H = -382 \text{ kJ}$$

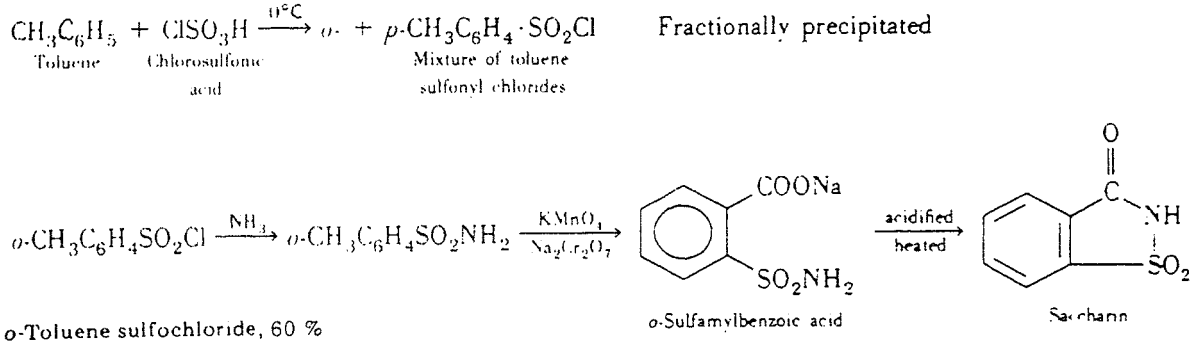
It is claimed that a catalyst mixture of 93% uranium oxide and 7% molybdenum oxide gives relatively high yields.

LIQUID PHASE

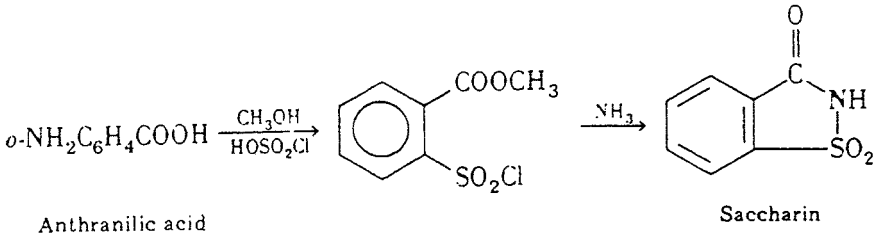
$$C_6H_5CH_3 \xrightarrow[40°C]{MnO_2,H_2SO_4} C_6H_5CHO + H_2O$$

Saccharin USP (o-benzosulfimide) is approximately 500 times sweeter than sugar. It has been widely used by diabetics and in diet drinks and foods. However, in 1972 the FDA

removed saccharin from the Generally Recognized as Safe (GRAS)[10] list and required that all food and beverages containing saccharin have a warning label. A study was undertaken by the National Academy of Sciences to determine its safety for human consumption, but it did not provide definite conclusions.[11] In 1977 the FDA restricted the use of saccharin, a decision based on limited test data on laboratory animals. Saccharin is manufactured, employing the following reactions, with a 90 percent yield on the last step.



An alternate synthesis from anthranilic acid is claimed to yield a product with less bitter aftertaste.



Miscellaneous Processes. *Aspartame,*[12] 1-aspartyl-1-phenylalanine, is 200 times sweeter than sugar. It has recently won limited approval from the FDA for use in some foods, and for use in soft drinks. It now is able to compete in the nonnutritive sweetener market with saccharin, which has been on the market for many years.[13] The regulation that requires a warning label on saccharin-containing foods will expire in 1983, and, unless it is extended, aspartame will be the only accepted nonnutritive sweetener on the market. Saccharin consumption is about 7 g per capita per year, and 3 to 4 $\times$ 10^3 t/year is produced, so the market is large.[13a] A combination of saccharin and aspartame is sweeter than either compound alone and aspartame has no objectionable aftertaste as saccharin does. Aspartame, however, is not very stable to heat and liquids, but it will retain its sweet taste in soft drinks for about 6 months.

Terpineols are among the cheapest synthetics and are widely used in soap because of their woodsy and floral odors. Formerly, all terpineols were made from turpentine oil, which consists largely of α-pinene, but recently pine oil has become an important source. Terpineols

[10]Hall, GRAS—Concept and Application, *Food Technol.* 29 (1) 48 (1975).

[11]National Academy of Science Report No. PB-238137/AS, 1975 (available from National Technical Information Service, Springfield, Va.).

[12]For saccharin and aspartame, *Food Eng.* 54 (7) 77 (1982).

[13]Sugar Substitutes Seek Sweet Smell of Success, *Chem. Eng. News* 52 (44) 37 (1974), *Food Eng.* 46 (8) 27 (1974).

[13a]t = 1000 kg.

may be manufactured directly in a one-step process from pinene by reaction with sulfuric acid and acetone for 6 h at 35 to 40°C. The product is purified by fractional distillation. The two-step method has an advantage in that the purification of the intermediate, terpin hydrate, is easier than that of terpineol. Terpin hydrate is formed by reacting pinene with dilute sulfuric acid and an emulsifying agent. The purified hydrate is dehydrated to terpineol by oxygenated carboxylic acids. Terpineols are separated from pine oil by fractional distillation.

Menthol has long been extracted as the levo from from oil of Japanese peppermint and used in cigarettes and many other products as an antiseptic cooling flavor. The pure optically active form is made by Glidden Co. from β-pinene (from turpentine).[14] This compound is hydrogenated, isomerized, and dehydrogenated to make β-citronellal. Catalytical conversion produces isopulegol, and hydrogenation yields *l*-menthol, after fractional distillation and crystallization.

The acetals of aldehydes have an odor only slightly modified from that of aldehydes but have great alkali resistance. Hence these acetals are used in soaps, which are very difficult to perfume.

Perfume Formulation

An actual example of a compound perfume similar to a widely sold product (Table 1.2) indicates the various components that have been discussed and shows their use in a blended product. The foundation odors are from eugenols, methyl ionone, and bergamot oil. Although the formulation given in the table shows a lower number, a single fragrance may contain 50 to 100 different compounds and subcompounds; in fact, as many as 300 ingredients may be used. Approximately 500 natural and 3000 synthetic oils are available for perfume production.[15]

FRAGRANCE QUALITY. The majority of domestic perfume houses do not manufacture their own scents; they usually import natural floral oils and have their synthetics custom-made by

[14]Chemicals from Trees, *CHEMTECH* 5 (4) 235 (1975).

[15]Aerosols; Fragrance Front-Runners, *Chem. Week* 86 (1) 24 (1960).

Table 1.2 Composition of a Perfume

Component	Grams	Component	Grams
Essential oils		Synthetics	
Sandalwood oil	10	Coumarin	27.5
Bergamot oil	117.5	Vanillin	20
Ylang-ylang oil	40	Benzyl acetate	30
Petigrain oil	10	Oleoresin, opopanax	2.5
Orange flower oil	10	Balsams (resinoids)	
Rose otto	15	Tolú	5
Jasmine absolute	20	Peru	7
Isolates		Benzoin	70
Eugenol (from clove oil)	90	Animal fixative, castor tincture 1:10	12.5
Santalol (from sandalwood)	15	Synthetic fixatives	
Semisynthetics		Musk ketone	32.5
Isoeugenol (from eugenol)	110	Musk ambrette	12.5
Heliotropin (from safrole)	15	Vehicle, ethyl alcohol	450 kg
Methyl ionone (from citral)	237.5		

Table 1.3 Types of Perfumes

Classification	Manufacturer	Trade Name
Straight floral	Coty	Muguet des Bois
Floral bouquet	Revlon	Charlie
Aldehydic floral	Chanel	Chanel #5
Oriental	Coty	L'origon
Chypre	Factor	Acquamarine
Woody	Jovan	Sport Scent
Green	Shulton	Old Spice Herbal
Citrus	Jovan	Eau Fresh
Cougere	Dana	20 Carats
Canoe	Faberge	Brut
Musk	Jovan	Musk Oil
Spice	Shulton	Old Spice

aromatic firms. As the perfumer's skill and resources increase with experience and research, new equipment is developed for identifying fragrance components, even in trace quantities, such as infrared and ultraviolet spectrographs and chromatographs. Eventually, such instrumentation will be perfected to expedite production, but currently the perfumer's nose is regarded as the more discriminatory in arriving at a creative blend of exotic ingredients. Even he or she does not know precisely what will make one formulation successful where several hundred others may fail. Furthermore, after months of trial to attain certain objectives, a consumer panel may be unenthusiastic about the product. High quality from batch to batch is routinely ensured by standard tests, such as specific gravity, optical rotation, refractive index, acid number, and ester number. Provided success is met thus far, "the name, the package, the advertising must all be perfectly orchestrated" with the product.

The psychological effect of odor is successfully used primarily to increase customer appeal. Perfumed merchandise outsells its odorless counterpart by a large margin. An insurance company increased its sales of fire insurance overnight by sending out advertising blotters treated to simulate the acrid odor of a fire-gutted building. All kinds of paper are now perfumed to increase sales appeal. Table 1.3 lists the main types of perfumes.

THE FLAVORING INDUSTRY

There are only four basic flavors which the nerve endings in the taste buds on the tongue can detect: *sweet, sour, salty,* and *bitter.*[16] The popular conception of flavor, however, involves the combination of these four basic stimuli with concurrent odor sensations. Apple, for instance, tastes merely sour, with a trace of bitterness from the tannins present. The main concept received of an apple is due to the odor of acetaldehyde, amyl formate, amyl acetate, and other esters present in the volatile portion. The principles of perfume blending also hold good for flavor manufacturing. The best flavoring essences are natural products altered and reinforced where necessary by synthetics. In addition to alcohol as a vehicle, glycerin and isopropyl alcohol are used for liquid preparations, and emulsions of bland gums, such as tragacanth and acacia (gum arabic), for pastes. The same fixatives are employed, especially vanillin and coumarin; animal types are used sparingly. Many essential oils find application

[16]Hornstein and Teranishi, The Chemistry of Flavor, *Chem. Eng. News* 45 (32) 93 (1967).

in the flavor industry, the more common being spice oils, citrus oils, peppermint, and spearmint. Almost all perfume synthetics find acceptance, plus a number made especially for flavors. The esters of ethyl, methyl, amyl, propyl, and benzyl alcohols with acetic, propionic, butyric, salicylic, caproic, formic, valeric, and anthranilic acids are widely used to characterize fruit flavors. As with flower perfumes, many chemical specialties keynote individual fruit aromas. The γ-lactone of undecylenic acid is a true representation of the fresh odor of a cut peach. A strawberry base is the ethyl ester of methylphenylglycidic acid, although it is not a true effect and partakes of a somewhat unnatural tone. Anethole has the taste of anise and licorice, benzyl acetate tastes like raspberry or cherry, and allyl caproate is used for pineapple flavors. Other common compounds used for flavorings are cinnamaldehyde (cinnamon), diacetyl (butter), menthol (mint), and isoamyl acetate (banana).

Natural Fruit Concentrates

Although the essential oils used in flavoring are the same grade and source as those used for perfumes, fruit flavors are handled in a somewhat different manner. Because of the large percentage of water in most common fruits (from 75% in the banana to 90% in the strawberry) and the presence of considerable amounts of sugar and other easily fermented materials, special processes must frequently be employed, such as the following:

Distillation and extraction of the fruit. The ripe fruit is stoned and comminuted. It is then subjected to steam distillation and rectification until all the aroma is concentrated in a small portion of the aqueous distillate. This portion is then extracted with low-boiling petroleum ether, and the ether removed under vacuum to leave an *essence*, or *quintessence*, of the fruit used. Cherry, apple, strawberry, and raspberry are treated by this method.

Extraction of the juice. In this system the expressed and filtered juice is extracted directly without previous distillation. Occasionally, the juice is allowed to ferment slightly before extraction. This is supposed to result in a fuller flavor.

Concentration of the juice. The expressed and filtered juice is concentrated in vacuum evaporators with a low degree of heat until the water is largely driven off and the sugar concentration is high enough to inhibit bacterial growth (60%). This type of concentrate often has a "jam," or cooked flavor, especially in the case of the strawberries. An alternative method of concentration is freezing. After reducing the temperature sufficiently, the mush of practically pure water ice is filtered off, and the partly concentrated juice is refrozen and refiltered until the requisite strength is obtained. This is the *optimum* method of producing concentrates, since there is little injury from heat, and the slight off-flavors from oxidation can be avoided by running the process in an atmosphere of carbon dioxide.

VANILLA. The vanilla bean is grown principally in Madagascar, Tahiti, and Mexico. It is the immature fruit of the orchid *Vanilla planifolia* and is cultivated as a vine on trees which support it. The pods are picked when they are just starting to turn from a uniform green to yellow at the tip and have a rather disagreeable odor. The green pods undergo a curing treatment of from 3 to 5 months' duration. The cured bean is pliant, shiny, and dark-colored. The odor has become full and rich, and the treatment may have left white aromatic crystals on the outside of the bean. What has happened is that the glucoside glucovanillin, present in the bean, has been acted upon by a ferment and split into glucose, vanillin, and other aromatics. Substances identified in the vanilla bean are anisic acid, alcohol, and aldehyde; vanillic acid and alcohol; cinnamic acid and its esters; vanillin, ethyl vanillin, and possibly other homologs of vanillin.

Preparation of vanilla extract. One hundred pounds of a blend of Mexican and Bourbon beans is finely cut up and macerated cold, with three successive portions of 35% ethyl alcohol of 45 kg each. These extracts are combined to make a fine vanilla extract. Other solvents may be used, and the extraction carried further, but the product is coarser and less desirable as a fine flavor (cf. Fig. 1.6).

CHOCOLATE AND COCOA. The cacao bean, the seed of *Theobroma cacao* L. grows in equatorial areas on the tree in pods with from 30 to 60 beans. The pods are split open, and the watery pulp containing the seeds is allowed to ferment in boxes from 2 to 7 days, which, in addition to liquefying the pulp, kills the embryo (46°C), reduces the toughness of the bean, frees theobromine from the glucoside, and reduces the astringent tannin content. This fermentation is necessary for flavor in the final product. The fermented beans are dried and shipped to manufacturing centers. The beans are then heated in rotary roasters between 105 and 120°C, which develops the true chocolate flavor and aroma, removes unpleasant tannins and volatile matter (butyric and acetic acid, organic bases, and amines), dextrinizes the starch, and embrittles the husk. The roasted beans are quickly cooled to prevent overroasting, cracked in a conical mill, dehusked by a winnowing air stream, and degerminated. This product is known as *cacao nibs.* To work up the cacao product into chocolate, the modern method is to grind sugar in a closed-circuit disintegrator and the nibs in a separate water-cooled two-stage disk mill with closed-circuit removal of the fines. The two are then mixed. This method produces a fine, uniform product. The paste is run through a concher, which is a granite bed with reciprocally acting granite rollers. It reduces the particle size to an average of less than 1 μm. It is steam-heated to run at 57°C or can be allowed to heat itself by friction (50°C). Milk chocolates are prepared by adding condensed fresh milk or milk powder to the mill (melangeur). The finished product has a cocoa-butter content of 30 to 35% and not less than 12% milk solids. For cocoa, the roasted and ground beans are subjected to pressure in hydraulic presses to remove some of the fat content. Whereas originally roasted beans contain 55% fat, the product remaining after this treatment has the fat reduced to 20%, and is known as *cocoa.* The removal of fat makes a beverage that is not too rich and one in which the fat does not separate on top.

MONOSODIUM GLUTAMATE (MSG, $COOH(CH_2)_2CH(NH_2)COONa$). This compound is an important flavoring agent, yet has no flavor of its own. It accentuates the hidden flavors of food in which it is used. Reports that the use of MSG in foods is harmful were denied by a National Academy of Science—National Research Council report in 1971.[17] In 1974 the Food and Agricultural Organization of the World Health Organization approved the use of MSG as safe. Glutamic acid exists in three forms, but only the monosodium salt of L-glutamic acid has a flavor-accentuating capacity. Although glutamic acid is a constituent of all common proteins, the economical sources have been wheat gluten, corn gluten, and Steffens filtrate. When Steffens beet-sugar wastes are used, the principal steps involved are (1) concentration and collection of the Steffens filtrate, (2) its hydrolysis, usually with caustic soda, (3) neutralization and acidification of the hydrolysate, (4) partial removal of the inorganic salts, and (5) crystallization, separation, and purification of the glutamic acid. MSG is made from the acid as described above. The present production of MSG is largely from fermentation,[18] and a

[17]*Chem. Eng. News* 49 (28) 17 (1971).

[18]New Processes, *Chem. Eng.* 69 (16) 17 (1962); *Ind. Eng. Chem.* Annual Unit Processes Reviews: Fermentation, from 1961 on; Hoelscher, Fermentation, *Chem. Eng.* 71 (8) 91 (1964); ECT, 3d ed., vol. 2, 1978, p. 410.

flowchart is presented in Fig 1 .7. Several U.S. companies have developed their own microbiological process or obtained it from the Japanese. The raw material is frequently dextrose or sugar. However, the Japanese are using a synthetic process based on acrylonitrile

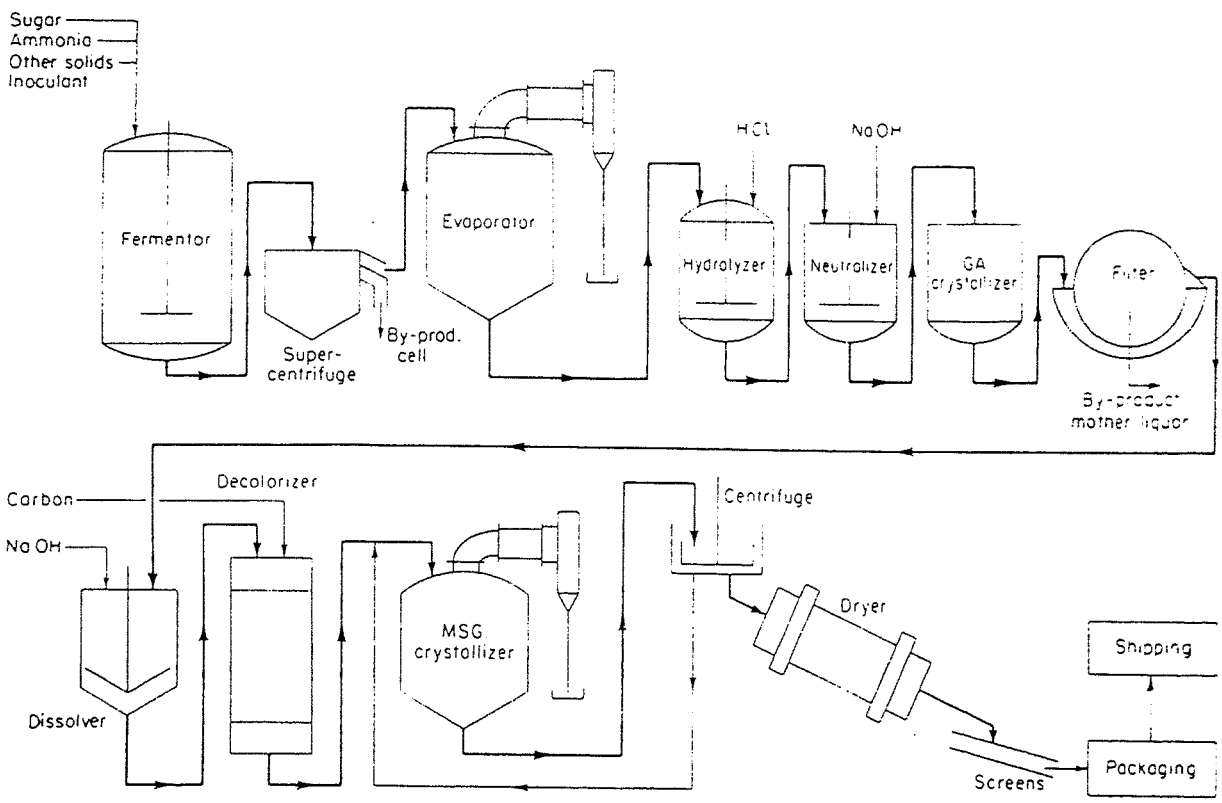
Flavor-Essence Formulation[19]

Formulas are given in Table 1 .4 for a fruit flavor used in gum manufacture and a natural apricot flavor. These show how a well-balanced flavor may be made up of natural products reinforced with suitable synthetics as well as a wholly natural formulation. Many formulas are to be found in print which consist mainly of esters of synthetic origin. These are harsh and unnatural, and, in many cases, the only resemblance to the original is in the designation of the flavor.

FOOD ADDITIVES

"The food revolution in progress since the turn of the century almost defies description. The evidence is all around us—on fertile farm lands, and in lush orchards, among grazing herds

[19]Mussinan, Analytical Chemistry and Flavor Creation, *CHEMTECH* 10 (10) 618 (1980).



To produce 1 t of MSG·H_2O, the following materials and utilities are required:

Sugar	1.5–2.5 t	Fuel	46.4 MJ
Electricity	79,200 MJ	Direct labor	17.6 work-h

Fig. 1.7. Flowchart of monosodium glutamate production by fermentation. *(International Minerals and Chem. Corp.)*

***Table* 1.4** Typical Flavors

Artificial Fruit Flavor for Chewing Gum			
	%		%
Heliotropin	0.05	Oil of lemon	5.00
Ethyl vanillin	1.00	Oil of tangerine	5.00
Vanillin	2.00	Ethyl acetate	16.40
Aldehyde C_{16}	0.55	Ethyl butyrate	15.00
Oil of cloves	1.00	Isoamyl acetate	10.00
Oil of peppermint	2.00	Isoamyl butyrate	5.00
Oil of orange	37.00		

Natural Apricot Flavor			
	%		%
Apricot juice conc.	99.6	Oil of orange	0.1
Absolute carob	0.1	Oil of petitgrain	0.05
Vanilla extract	0.1	Oil bitter almond	0.05

and loaded refrigerator trucks and railroad cars, in magnificent food stores and, finally, in kitchens and on dining tables at home or in restaurants."[20] The food industry, estimated at over \$200 × 10^9 yearly, is the country's *largest business*. The average family spends approximately 18 percent of its income on food. (See Chap. 25, Food and Food By-Product Processing Industries, for details on the size of this industry.) Food additives are those chemicals combined with foods by the manufacturer to effect certain modifications involving preservation, color, flavor enhancement, and stabilization, which have helped to make an astounding improvement in our food supply, as well as alleviating work in the kitchen. Additives are as old as history itself, spices, for example. *Intentional additives* are substances added in carefully controlled amounts to preserve the quality of food, improve its nutritive value, or add flavor, for example, MSG (Fig. 1.7). Common kitchen staples such as vinegar, starch, and salt are in this category. *Incidental additives* are those that, although having no function in finished food, become part of it through some phase of production, processing, storage, or packaging.

The food additives have been separated into 52 categories.[21] This list ranges from acidulants, anticaking (drying) agents, baking aids (yeast foods) through flavors, flavor enhancers, starch modifiers, nonnutritive sweeteners to preservatives, sequestrants (chelating agents), stabilizers, vitamins, and wetting agents. The main classifications[22] are colors, 3 percent; flavors, 16 percent; enzymes, 8 percent; acidulants, 8 percent; nonnutritive sweeteners, 2 percent; surfactants, 10 percent; antioxidants, 3 percent; preservatives, 4 percent; flavor enhancers, 7 percent; vitamin supplements, 3 percent; and nonspecialty additives such as soy concentrates, carrageenin, alginates, and leavening agents, 36 percent.

Commonly used additives include chemical preservatives like propionic acid and benzoic acid; *buffers* and *neutralizing agents*, such as acetic acid and sodium citrate; *emulsifying*

[20]*Food Additives Codex, 1972*, Manufacturing Chemists Association; Furia, *Handbook of Food Additives*, Chemical Rubber, Boca Raton, Fla., 1968; Fernandez, Mixing Technology and Food, *New Eng.* 3 (11) 52 (1974); ECT, 3d ed., vol. 11, 1980, p. 146.

[21]*Food Ingredients Directory*, Intechmark Corp., Palo Alto, Calif.

[22]Another Checkup for Additives, *Chem. Week* 127 (17) 29 (1980).

agents like polysorbates; *nonnutr ve sweeteners*, such as saccharin; *nutrients*, among which are ascorbic acid and other vitam s; and *thickeners* like agar-agar and acacia. Here should be included *spices* like allspice and nger and, finally, essential oils (Table 1.1) such as bitter almond and lemon. Some of these ldditives are permitted to be used freely, and others in limited amounts.

The FDA is conducting an on-go ; review of the GRAS list of substances. Contrary to popular reports, governmental regu ation concerning safety in food products is not completely biased on the side of the food industry.

It is useful in gaining perspective on the use of food additives to realize that the average person consumes 680 kg of food per year, and of that only 63 kg are food additives. Of the 63 kg, 58.5 kg are composed of sugar, salt, corn syrup, and dextrose which are all normal, natural foods.[23] Leavening agents or substances used to adjust the acidity account for 4 kg, which leaves only about 0.5 kg of other additives. These are divided among about 1800 different substances. Food additives play an invaluable role in preserving food and add greatly to its variety, stability, flavor, abundance, and appearance. For any new food additive the FDA requires submission of a Food Additive Petition (FAP) which must contain documented information on safety, declaration of intended use(s), efficacy at specific levels in the food system, manufacturing details including intermediates, and an environmental impact statement. It has been estimated that it can easily cost $1 million just to obtain FDA approval. Because of this high cost, less than a dozen new products have been approved in the last 20 years. Most of the additives used have been approved for years, but the FDA is currently engaged in requiring the retesting of many of them.

NATURAL ACCESSORY CHEMICALS. Foodstuffs contain small amounts of accessory chemicals, including vitamins (Chap. 6), chelating agents, and natural antioxidants. Carbohydrates consist of various sugars, starches, dextrins (Chap. 30), celluloses, and gums. Proteins are composed of amino acids. Shortenings contain esters of palmitic, oleic, linoleic, and stearic acids. Natural foodstuffs contain substances of no known nutritive value, as well as substances that are harmful if taken in larger amounts than are normally used; for example, coffee and tea contain caffeine, whose pharmacological effect is well known. Even small amounts of arsenic and other toxic metals are found in food.

Potatoes contain so much solanine (a deadly poison) that if the amount consumed by the average person in a year was concentrated into a single dose, it would be sufficient to kill a horse. The list could be extended greatly, but it is sufficient to realize that "natural" foods are not necessarily better or safer than properly prepared food containing carefully tested and controlled additives.

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[23]If It's Natural, How Good Is It? *Food Eng.* 54 (3) 7 (1982).

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Chapter 2

Oils, Fats, and Waxes

At present about 11.7×10^6 t of edible vegetable oils and about 4.2×10^6 t of edible animal fats and oils are produced in the United States each year.[1] About 7×10^6 t are exported and the remainder is consumed in the United States.

Figure 2.1 depicts the relative consumption by the food, soap, and paint industries of various oils and fats. It also shows the direct competition of the chemical, soap, and paint industries with basic food production. Three types of agricultural products make up the bulk of the farm products that enter into the chemical process industries. Animal fats, both edible and inedible materials, are the largest in quantity and value. Starch (Chap. 30) runs a close second, and vegetable oils are next.[1a] Fats and oils are found widely distributed in nature, in both the plant and animal kingdoms. Waxes likewise are natural products but differ slightly from fats and oils in basic composition. Whereas fats and oils are mixtures of the glycerides of various fatty acids, waxes are mixed esters of higher polyhydric alcohols, other than glycerol, and fatty acids.

Table 2.1 indicates the characteristic composition of various important oils in regard to their fatty acid content. These acids have an even number of carbons and fall within (1) the saturated series, as exemplified by stearic acid, which is the basis for nondrying oils, (2) the monoolefinic acids, with one double bond between carbons as illustrated by oleic acid, and (3) the polyolefinic series, with more than one such double bond, as exemplified by linoleic and linolenic acids. The latter two classes of acids, being unsaturated, furnish semidrying and drying oils, according to the amounts of unsaturation present. The chief constituents of vegetable oils are 16- and 18-carbon acids, and 20-, 22-, and 24-carbon acids predominate in fish oils. Coconut oil is unique in that it consists of esters of much shorter carbon-chain acids, 12- and 14-carbon acids being present in the greatest amount.

There is a growing, recent demand for polyunsaturated oils in food products; the largest in supply, soybean oil, has 61% polyunsaturated constituents; safflower oil contains 68%; corn oil, 42%; cottonseed oil, 50%; peanut oil, 21%; and olive oil, 7%. The degree of saturation of the acids involved affects the melting point of the ester mixture; the more unsaturated acids give esters with lower melting points, and these are the chief constituents of oils. The more saturated esters, on the other hand, are constituents of fats. Thus we see that the factor determining if one of these compounds is termed a fat or an oil is merely its melting point. These oils are called fixed oils, in distinction from the essential, or volatile, oils described in Chap. 1. Fixed oils cannot be distilled without some decomposition under ordinary atmospheric pressure. Differentiation should also be noted from petroleum oils, discussed in Chap. 37.

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[1] t = 1000 kg.

[1a] *Statistical Abstract of the United States*, 1981; *J. Am. Oil Chem. Soc.* 59 (1) 7A (1982).

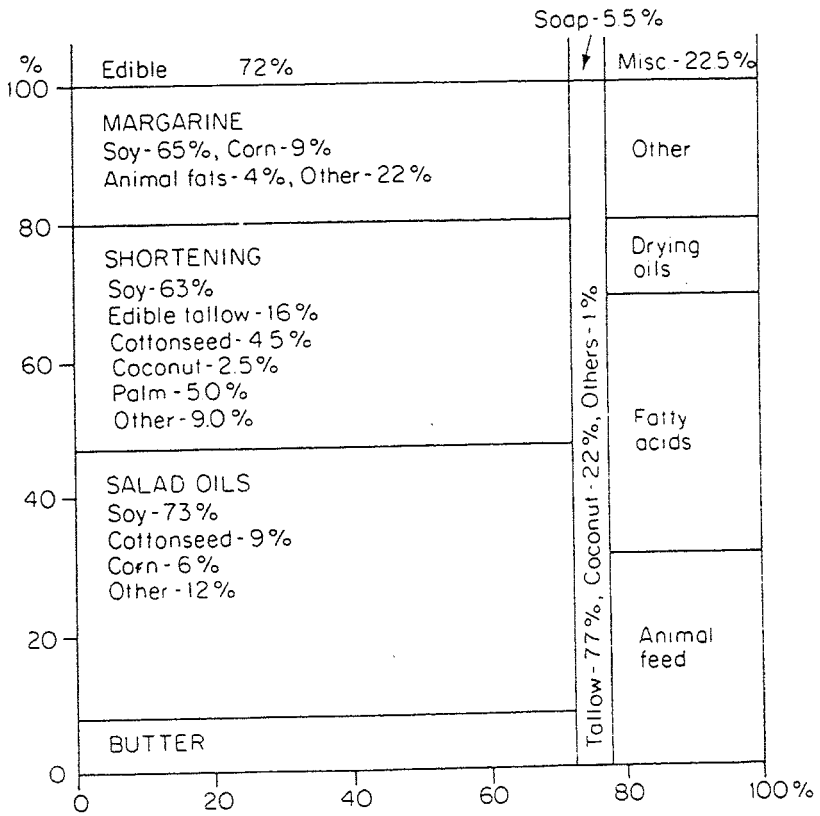


Fig. 2.1. Consumption of fats and oils by various industries, 1980.

HISTORICAL. Since ancient times humans have known how to remove oils and fats from their natural sources and make them fit for their own uses. Animal fats were first consumed as food, but it was not long before they were burned for light and heat. Obtaining oils from vegetable sources is of ancient origin, for the natives in the tropical regions of the globe have long been removing these oils from various nuts after drying them in the sun. The utilization of marine oils began with the whaling industry, which was started by the Basques in the Bay of Biscay in the fifteenth century.

The first chemical reaction applied to fats and oils (excluding oxidation in burning) was that of saponification, to give soap. The early raw materials were mainly of animal origin, the rendering of animal flesh being an old art. The industrialization of oils and fats began with the erection of a cottonseed mill in South Carolina, about 1826. This crude industry did not expand very rapidly until after 1865. In 1850, the use of caustic soda to remove free acids from oil was introduced from France. About this time, the millers became aware of the value of the linters that clung to the hulls, and also of the hulls themselves, for cattle feed. The beginning of the oleomargarine (margarine) industry in Chicago in 1885 gave impetus to the cottonseed-oil industry. The higher quality demanded by this new market produced several processing improvements. Fuller's earth was used to decolorize the oil. In 1893, it was learned that the oil could be deodorized by blowing steam through it at high temperatures. Later it was found that deodorization under reduced pressure improved both flavor and odor. In 1900 the discovery that oils could be upgraded by *hydrogenation* to produce fats revolutionized the entire oil and fat industry and led to hydrogenated shortenings. This discovery also made many of the lesser-known oils marketable. This phase of the industry has advanced until now much shortening is made by hydrogenating unsaturated oils and fats to a higher degree of saturation than originally found, but rarely to total saturation.

Table 2.1 Fatty Acid Content of Various Oils and Fats (in percentage)

No. of C Atoms	Acid	Formula	Butter	Cotton	Soybean	Corn	Menhaden	Whale	Linseed	Coconut	Beef Tallow	Lard
4	Butyric	C_3H_7COOH	4.0	—	—	—	—	—	—	—	—	—
5	Caproic	$C_5H_{11}COOH$	2.0	—	—	—	—	—	—	—	—	—
8	Caprylic	$C_7H_{15}COOH$	1.0	—	—	—	—	—	—	8.0	—	—
10	Capric	$C_9H_{19}COOH$	2.5	—	—	—	—	—	—	7.0	—	—
12	Lauric	$C_{11}H_{23}COOH$	3.0	—	—	—	—	—	—	48.0	—	—
14	Myristic	$C_{13}H_{27}COOH$	10.0	0.6	—	—	7.0	8.0	—	17.5	3.0	1.0
14	Myristoleic	$C_{13}H_{25}COOH$	—	—	—	—	—	1.5	—	—	—	0.2
16	Palmitic	$C_{15}H_{31}COOH$	25.0	22.9	8.3	7.5	16.0	12.1	6.5	8.8	28.0	28.0
16	Palmitoleic	$C_{15}H_{29}COOH$	—	—	—	—	17.0	15.0	—	—	—	3.0
18	Stearic	$C_{17}H_{35}COOH$	11.0	2.2	5.4	3.5	1.0	2.3	4.5	2.0	25.0	13.0
18	Oleic	$C_{17}H_{33}COOH$	28.5	24.7	24.9	46.3	27.0	33.4	20.9	6.0	42.0	46.0
18	Linoleic	$C_{17}H_{31}COOH$	2.5	49.7	52.7	42.0	—	—	17.4	2.5	2.0	6.0
18	Linolenic	$C_{17}H_{29}COOH$	—	—	7.9	—	—	9.0	50.6	—	—	0.7
20	Arachidic	$C_{19}H_{39}COOH$	—	—	0.9	0.5	—	—	—	—	—	2.0
20	Arachidonic	$C_{19}H_{35}COOH$	—	—	—	—	20.0	8.2	0.1	—	—	—
22	Clupanadonic	$C_{21}H_{35}COOH$	—	—	—	—	12.0	10.5	—	—	—	—
24	Lignoceric	$C_{23}H_{37}COOH$	—	—	—	0.2	—	—	—	—	—	—

USES AND ECONOMICS. Fats and oils have always had an essential role as food for humankind. In addition, however, our modern industrial world has found many important applications for them. The largest consumption of fats for chemical raw materials is in making fatty acids (Chap. 3), which have an estimated tonnage of 813,000 t/year. Oils are saponified, hydrogenated, epoxidized, and sulfonated to a great number of usable products, and fats are isomerized and interesterified, all to produce upgraded and more useful oils and fats. Table 2.2 gives some industrial uses of fats and oils.

There are two broad classifications for fats and oils: edible and inedible. The consumption of fats and oils in edible products represents about 72 percent of all uses of these materials and averages about 24 kg per capita. Various edible oils, cottonseed, olive, soybean, corn, etc., are employed for salad dressings, for other table uses, and for cooking purposes. Hydrogenated fats for cooking and baking, such as Crisco, may include a wide variety of vegetable oils, such as cottonseed, palm, and soybean, since the hydrogenating process *improves* the color, flavor, and odor of the original crude product as well as its keeping factor. Various fish-liver oils are used in the medicinal field for their vitamin content and in the paint industry as drying oils. Castor oil is a well-known cathartic.

In 1980, 28 percent of all oils and fats consumed in the United States was for inedible products, as shown in Fig. 2.1. About 18 percent was used in the soap industry, including tallow, coconut oil, palm oil, and certain greases. Some were slightly hydrogenated to make them suitable for soapmaking. The drying-oil industries (including paints and varnishes) consume 9 percent of all inedible oils, and other consumption of linseed oil, tung, soybean, and castor is in smaller demand. These drying oils are essentially unsaturated and produce films or coatings upon oxidation. They are also employed with synthetic resins and cellulose derivatives to give special types of films. Castor, linseed, soybean, rapeseed, and cottonseed oils are being used to some extent as plasticizers for lacquers and polymers. Other miscellaneous uses include applications in the following industries: oilcloth and linoleum, chemical (for the manufacture of fat and oil derivatives), lubricant and grease manufacturing, printing, and tin plate. A wide variety of oils are included as integral parts of various polishes, creams, and emulsions. Large quantities of sulfonated glycerides and sulfated fatty alcohols and derivatives serve as wetting agents and detergents. Table 2.3 details the statistics of the principal fats and oils, together with some of their important derivatives. It should be compared with Fig. 2.1. *Waxes*, such as carnauba, beeswax, and candelilla, enter into the manufacture of various polishes for floors, shoes, automobiles, and furniture. Other outlets include the making of carbon paper, candles, electrical insulation, waterproof textiles, and phonograph records.

Table 2.2 Industrial Uses of Fats and Waxes

Fat or Oil	Use
Animal fats	Soaps, greases, paints, varnishes, syndets, fatty acids, and plasticizers
Coconut oil	Fatty alcohols, soaps, and detergents
Linseed oil	Paints, varnishes, floor coverings, lubricants, and greases
Soybean oil	Paints, varnishes, floor coverings, lubricants, and greases
Castor oil	Protective coatings, plastics, plasticizers, lubricants, hydraulic fluids
Tung oil	Paints and varnishes
Tall oil	Soaps, leather, paint, emulsifiers, adhesives, ink

***Table* 2.3** U.S. Production of Fats, Oils, and Derivatives, 1980 (in thousands of metric tons)

Vegetable		Fish	100
Soybean	8115	Derivatives	
Cottonseed	655	Salad oil	2200
Peanut	99	Shortening	1900
Sunflower	607	Margarine	1140
Safflower	36	Soap	423
Corn	373	Animal feed	656
Linseed	69	Paint and varnish	250
Animal		Fatty acids	813
Tallow and grease	3351		
Lard	454		
Butter	445		

SOURCE: *Statistical Abstract of the United States, 1981*, U.S. Dept. of Commerce; *J. Am. Oil Chem. Soc.* 59 (1) 8A (1982).

VEGETABLE OILS

Extraction of Oils

For purposes of discussion of the various technical aspects, the three classical divisions of the general subject of oils, fats, and waxes will be retained: vegetable oils, animal oils and fats, and waxes. Under each of these headings the general methods of manufacture will be discussed for the most important of the illustrative individual members. Table 2.4 indicates the yields of vegetable oils from some of the usual sources. The two general methods employed in obtaining vegetable fats and oils are expression and solvent extraction or a combination of the two. However, solvent extraction is increasing in use.[2] Solvent extraction has assumed importance in virtually all vegetable-oil recovery plants, alone or in combination with prepressing. For high-oil-content seeds, such as cottonseed and safflower seed, usually both expression and extraction are utilized in the recovery systems for higher yields.[3] Obtaining crude vegetable and animal oils involves primarily physical changes or unit operations, but chemical conversions are concerned in the refining and further processing of such oils.

COTTONSEED OIL. Figure 2.2 presents a flowchart for cottonseed and similar oils. The flowchart can be broken down into the following sequences of *unit operations* (hydrogenation will be considered under its own special heading):

[2]For cottonseed oil, expression by the *expeller*, followed by solvent extraction, has become the most practiced. The solvent extraction upgrades the oil and increases the yield, especially from damaged seed.

[3]Haines et al., Filtration-Extraction of Cottonseed Oil, *Ind. Eng. Chem.* 49 920 (1957) (flowsheet); Decossas et al., Cost Analysis (of preceding), *Ind. Eng. Chem.* 49 930 (1957); Brennan, Making the Most Out of Cottonseed Processing, *Chem. Eng.* 70 (1) 66 (1963); Tray and Bilbe, Solvent Extraction of Vegetable Oils, *Chem. Eng.* 54 (5) 139 (1947) (pictured flowchart); Witz and Hendrick, New Plant Puts Science into Cottonseed Processing, *Chem. Eng.* 71 (18) 48 (1964) (flowchart).

Table 2.4 Approximate Oil Yields of Certain Vegetable-Oil Materials

Raw Material	%	Raw Material	%
Babassu kernels	63	Palm kernels	45
Castor beans	45	Peanuts in the shell	30–35
Corn kernels	4	Peanuts shelled	45–50
Copra	63	Perilla seed	37
Cottonseed	15	Rapeseed	35
Flaxseed	34	Sesame seed	47
Hempseed	24	Soybeans	18
Kapok seed	18	Tung nuts	50–55

SOURCE: Mostly taken from U.S. Tariff Commission, *Fats, Oils, and Oil-Bearing Materials in the U.S.*, December 15, 1941. (Modified in 1977.)

Cottonseeds are cleaned by screening and aspiration. The lint is removed by passing the seeds through a series of linters (machines similar to cotton gins which operate on the saw-and-rib principle).[4] Each series of linters removes lint of different length, which is designated first-cut and second-cut lint. The lint cuts are aspirated and air-conveyed to separate lint beaters or cleaners which remove dirt and hull fragments from the lint before it is baled and sold.

The delinted seeds (blackseed) are cut or split in a bar-type huller, freeing the meats from the hulls, which are separated from the meats by screening and aspiration. The hulls thus removed are cleaned of attached meat particles in a beater and sent to storage for eventual consumption as roughage in animal feeds.

The meats are rolled into thin flakes (about 0.25 to 0.35 mm thick) to make them easily permeable to steam in the cooking operation; they are next cooked or conditioned in horizontal cookers at 110°C for 20 min before expression to rupture the oil glands, to precipitate the phosphatides, to detoxify the gossypol, and to coagulate proteins.[5] In direct solvent extraction, meats are conditioned before flaking.

The horizontal cookers are generally integrated with the expellers (Fig. 2.3); in prepress plants they are supplemented with a stacked cooker for additional heating capacity. The moisture is frequently raised to 12 to 14% and then gradually reduced to 5 to 7% in these units.

Most of the oil from the conditioned cottonseed is prepressed in mechanical screw presses with single or double worm shafts revolving inside a heavy perforated barrel and capable of exerting a pressure of up to 11.7 to 13.8 MPa (Fig. 2.3). (These have largely displaced the hydraulic presses previously used in cottonseed plants.) The oil removed by these presses is screened, cooled, filtered, and stored for refining. About 74 percent of all cottonseed is so

[4]Bailey, *Cottonseed and Cottonseed Products*, Interscience, New York, 1948.

[5]Dunning, Unit Operations in a Mechanical Extraction Mill, *J. Am. Oil Chem. Soc.* 33 (10) 465 (1956).

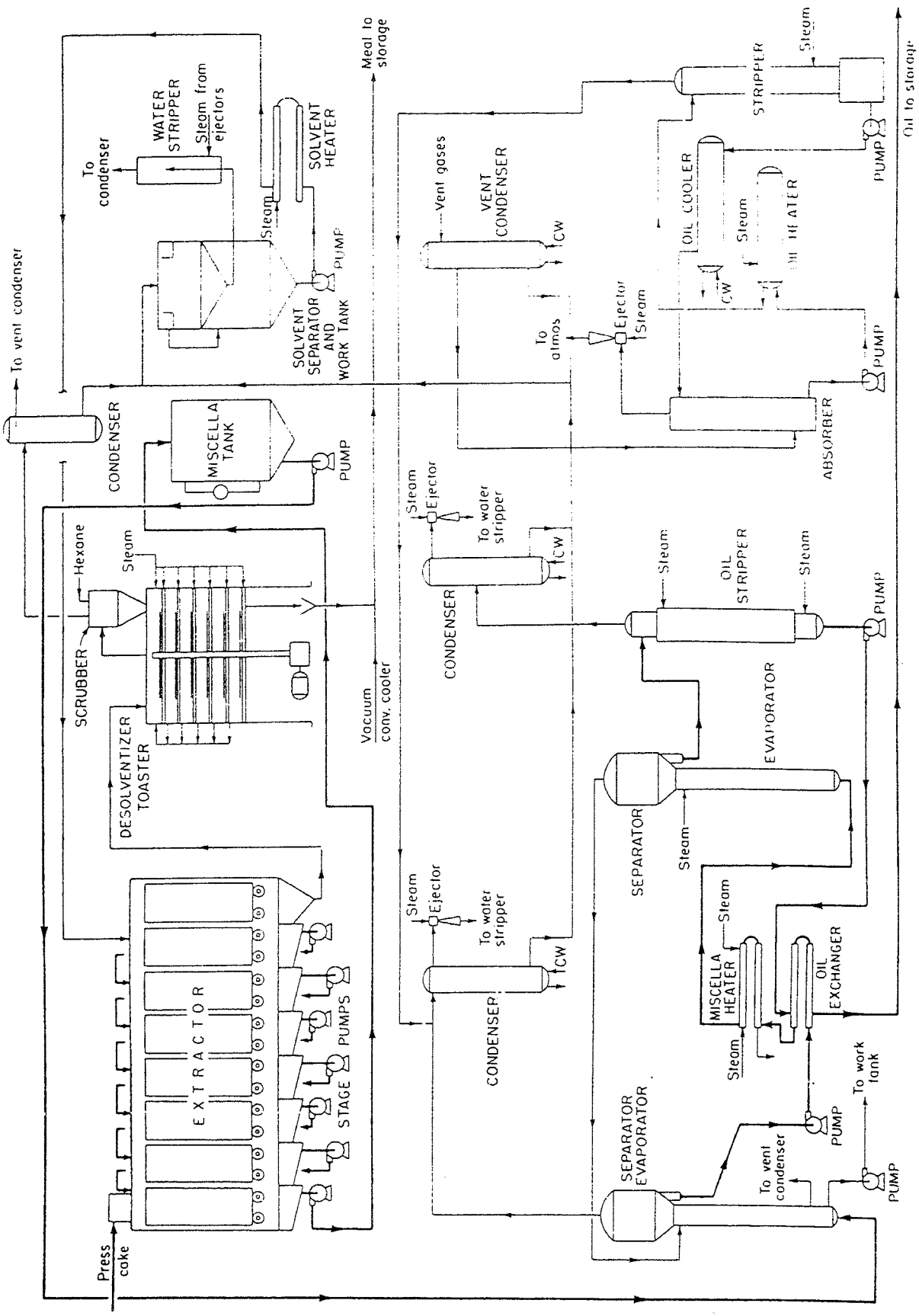


Fig. 2.2. Flowchart for cottonseed after pressing and flaking followed by solvent extraction with hexane, with a double effect evaporator to remove hexane from the cottonseed-hexane mixture (miscella), the first effect being heated by hexane vapor and the second by steam. The cells of the extractor are mechanically moved countercurrent to the hexane. *(The Austin Co.)*

processed; an additional 18 percent is processed by prepressing with solvent extraction and 8 percent by direct solvent extraction.

Solvent extraction recovers up to 98 percent of the cottonseed oil (Fig. 2.2), compared with 90 to 93 percent from screw-press expression alone. The soybean, which has a low oil content, but whose physical structure is particularly suited to solvent extraction (Fig. 2.4), has been responsible for this development. Solvent extraction has assumed importance in virtually all vegetable-oil recovery processes, alone or in combination with prepressing. In Fig. 2.2 the solvent hexane is sprayed onto flakes in buckets moving horizontally in the extractor[6] countercurrent to the hexane. The hexane dissolving the oil is known as miscella and is pumped to the evaporators, the first of which is heated by hot hexane vapor and steam from the toaster and the second by steam.

Virtually the entire cotton seed-oil production is used by edible-oil processors for shortening, margarine, and salad or cooking oils. The cake is broken or ground and used for cattle feed. The hulls provide roughage for livestock feeding. The linters which contain 70 to 85% α-cellulose are utilized as a cellulose source of high purity for rayon, plastics, lacquer, and explosives.

SOYBEAN OIL. Soybean-seed preparation differs slightly from cottonseed preparation. The weighed and cleaned seeds are first cracked between corrugated rolls, then conditioned without significant change in moisture in a stacked cooker or a rotary steam-tube conditioner, and finally rolled to thin flakes (about 0.25 mm thick). Solvent extraction can recover up to 98 percent of the oil, compared with about 80 to 90 percent from hydraulic or screw-press expression. Because of the efficiency of oil yields (hydraulic press, 14.5 kg/100 kg; screw presses, 15.3 kg/100 kg; solvent extraction, 18.2 kg/100 kg) virtually all new soybean installations today are solvent extractors. When solvent extracted, soybean flakes produce meal with a protein content of 44 to 46%, which can be increased by removing the soybean *hulls* before (front-end dehulling) or after (tail-end dehulling) solvent extraction. Front-end dehulling is accomplished by screening the cracked seed and removing the hull fraction by aspiration. Small meat particles are then separated from the hull stream on specific gravity separators. In the tail-end dehulling system the entire dried-meal stream is passed over specific gravity

[6]The V. D. Anderson Co., Cleveland, horizontal hydraulic basket extractor.

TABLE TO ACCOMPANY FIG. 28.2

	LABOR AND UTILITIES			
RAW MATERIALS	SEED HANDLING	SOLVENT EXTRACTION	PRODUCTS	WEIGHT, KG
Cottonseed, kg	1000	1000	Oil	173
Labor, work-h	7.7	1.5	Cake	482
Electricity, MJ	61	56	Hulls	185
Solvent (hexane) loss, L		2	Linters	104
Water, L	125*	250	Loss and trash	56
Steam, kg	288	495	Total	1000

**Recirculating cooling water.*

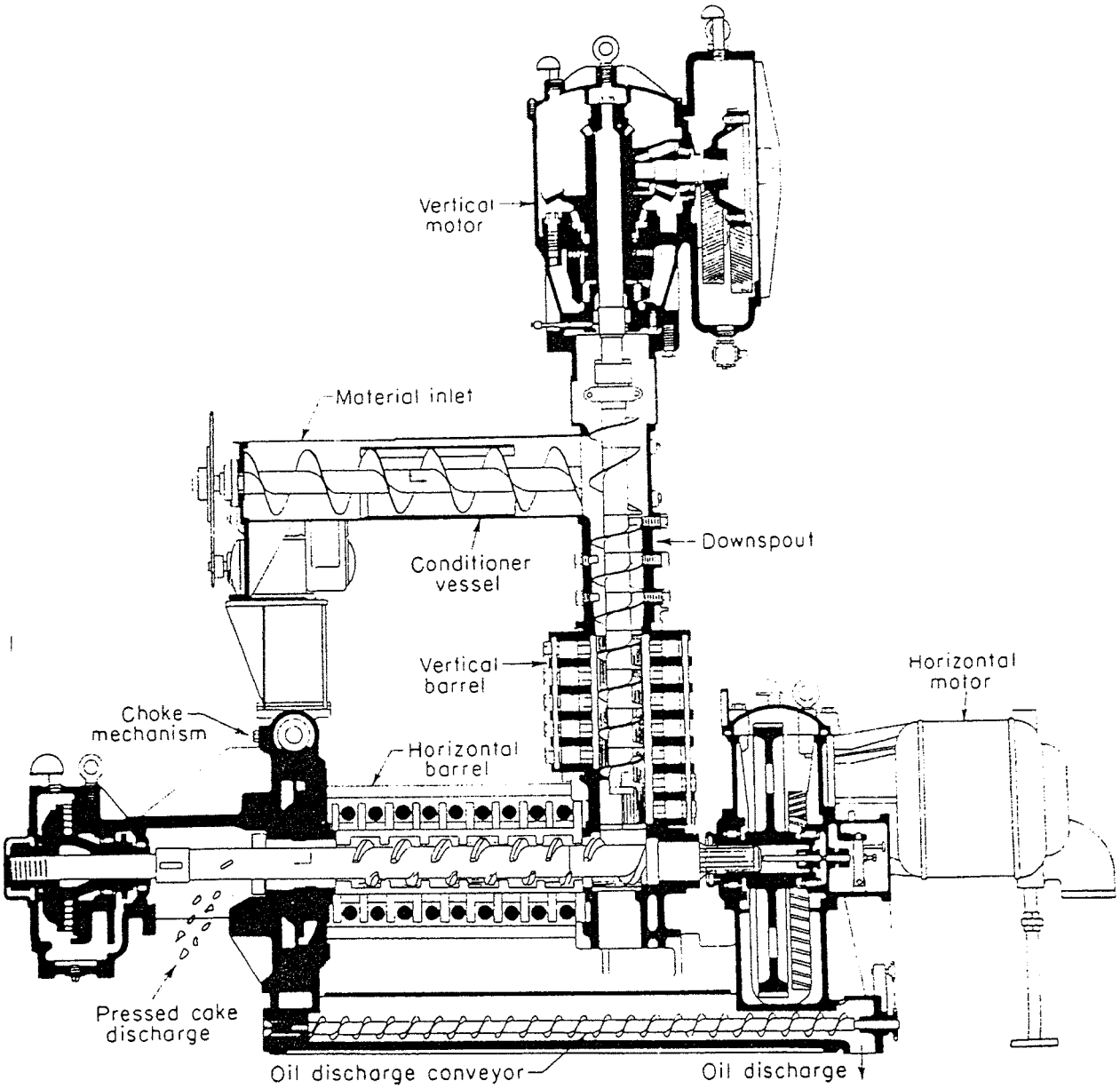
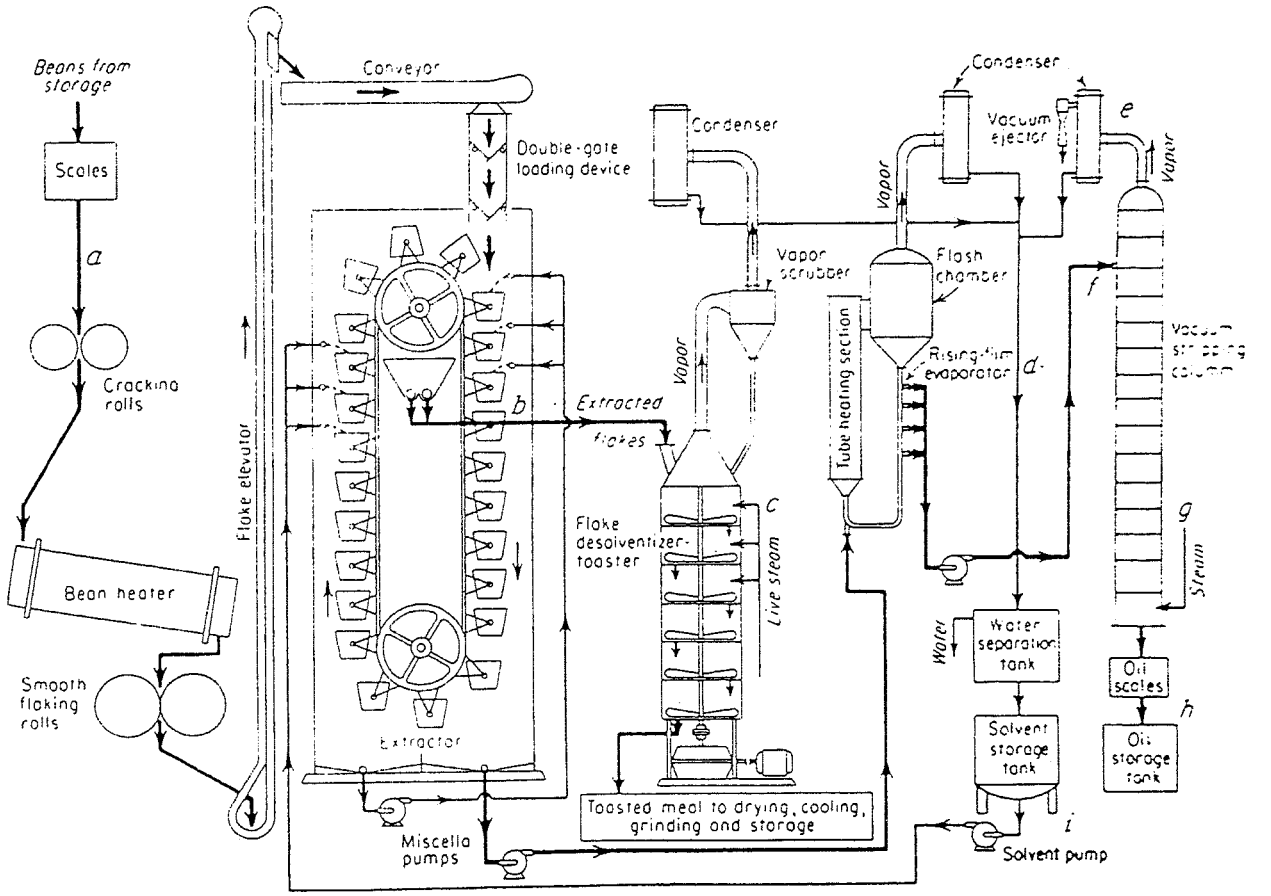


Fig. 2.3. Cutaway section of a twin-motor Superduo expeller. On cottonseed, the capacity is from 45 to 90 t per 24-h day, and for soybean about 24 t per 24-h day. To drive the propeller, 52 kW is required, and up to 4 boiler kW of steam is needed for the conditioner. *(V. D. Anderson & Co.)*

separators, producing two grades of meal, one containing 41% protein and the other containing 50% protein.

Solvent extraction[7] is carried out in a continuous countercurrent manner through a series of extraction stages. The extractors most commonly used in this country circulate solvent over the flakes, which are carried, usually in baskets, through the several extraction stages, the baskets moving in a circular, vertical, or horizontal direction. The vertical circular procedure, using hexane as solvent, is illustrated in Fig. 2.4. Although milling releases some of the oil, which is immediately dissolved in the solvent, the greater portion is removed by diffusion of the solvent through the cell walls until equilibrium is reached. By replacing the equilibrium solution with a solvent of lower oil content, the diffusion process is again resumed. The economical limit of this procedure is about 0.5% oil remaining in the seed mass. The rate of diffusion is directly proportional to the surface area of the seed particle and in an (inverse)

[7]Solvent Extraction of Oilseed, Chem. Eng. 58 (1) 127 (1951); Perry, 5th ed., p. 19–42.



UTILITIES, PER HOUR		QUANTITIES, KG/H
Steam	18,600 kg	In circulation at points marked
Power	4300 MJ	a. 37,650 beans, 12% moisture
Water (cooling)	378 m^3	b. 29,940 extracted flakes, 18,144 hexane
Labor	3 work-h	c. 4536 steam
Solvent loss	90 kg	d. 6800 oil, 19,500 hexane
		e. 680 hexane at 13.5 kPa abs
		f. 6800 oil, 680 hexane
		g. 272 steam
		h. 6800 oil
		i. 37,650 hexane

Fig. 2.4. Continuous flowchart for solvent extraction of soybeans.

power function of thickness with free circulation of the solvent. After extraction, the meal is toasted to increase its nutritive value. Solvent is usually removed from the miscella phase by passing it through a rising-film evaporator followed by a steam-stripping column. Double-effect, or dual, evaporators are frequently used, with one evaporator operated under vacuum and heated by vapor from the other stage or by vapor from the desolventizing toaster.[5] Solvent losses are usually minimized by venting the process noncondensables through a refrigerated vent condenser or an oil-absorption unit. The process crude oil produced is then stored for refining or sale. Dried and toasted meal from the solvent-extraction operation is ground to 10- to 12-mesh fines in a rotary pulverizer, screened, and stored for sale as feed.

[8]Milligan and Tandy, Distillation and Solvent Recovery, *J. Am. Oil Chem. Soc.* 51 347 (1974); R&D in Oilseed Routes, *Chem. Eng.* 89 (26) 21 (1982).

OTHER VEGETABLE OILS

Linseed oil. The flaxseed produced in this country is grown largely in the midwest, south Texas, and the far west. Production and refining are carried out by a process similar to that used for cottonseed oil, depicted in Fig. 2 .2, and Anderson expellers are first employed. The average oil content of the flaxseed is about 40%, which indicates a yield by expression of about 34 percent based on the weight of the seeds, leaving about 6% oil in the press cake. Newer and improved installations combine screw pressing with solvent extraction, reducing the residual oil in the cake to about 0.75%, as illustrated by Fig. 2.2.

Coconut oil. The raw material for the production of coconut oil[9] is all imported from various tropical countries, a large part coming from the Philippines. The raw material is brought in as copra, which is coconut kernel that has been shelled, cut up, and heat-dried at the point where grown. This treatment not only avoids the cost of shipping excess moisture, but also prevents deterioration of the oil. Coconuts, as they come from the tree, contain from 30 to 40% oil, and the copra contains from 65 to 70% oil. The copra is expressed in expellers or screw presses. A metric ton of copra yields about 800 kg of oil and 365 kg of cake. The oil is refined and contains from 1 to 12% free fatty acid, depending on the quality of the copra meats. Only oil of low free fatty acid content is employed for edible products, the rest (about 60 percent of the total receipts) being used for the production of soap and alcohols.

Corn oil. The production of corn oil differs from that of some of the other oils in certain respects. After cleaning, the corn is placed in large tanks and steeped in warm water containing SO_2, thus loosening the hulls from the kernels. The steeped corn is run through *attrition* mills, which break the germ away from the rest of the kernel. The separation of the germ and the kernel is accomplished by running the mixture into a tank of water, where the germ floats, because of its oil content, and is skimmed off. Before going into the ordinary grinding and expelling apparatus, the germ should be washed and thoroughly dried. The crude oil from the expellers (Fig. 2 .3) is given the usual purification treatment, such as that described for cottonseed oil. The oil content of the corn kernel, exclusive of the hull, is about 4.5%. This oil is used almost exclusively as a salad oil, with lower grades going into soap manufacture.

Palm oil. Palm oil is prepared from the fruit of the palm tree, which has been cultivated on plantations in Indonesia, the Malay Peninsula, and elsewhere. Palms grow naturally on the west coast of Africa. The fruit is 2.5 to 5.0 mm long and oval-shaped and weighs about 6 to 8 g on the average. The oil content ranges from 40 to 50% of the kernel, or seed. The oil is obtained in two separate procedures. In the first, it is removed from the fruit, and in the second from the kernels, or seeds. The former is done at the place where the fruit is grown. The procedure consists in cooking the fruit in large steam-pressure digesters equipped with agitators. From the steaming the charge goes to basket centrifuges, where a 10-min treatment, accompanied by blowing with live steam, separates the oil. The residual fiber and kernels are dried in a continuous rotary dryer and separated by a screening operation. The nuts, or kernels, are bagged and shipped to the United States, where they are processed by the methods previously described for oil removal. The fibers are burned under the boilers of the first processing plant. In the United States most of this oil goes into soap manufacture.

Peanut oil. Peanut oil is produced by either the hydraulic press or the Anderson expeller, from deskinned peanuts grown in the various southern states. The cold, first expression (about 18 percent) is edible, and some is hydrogenated. The oil is hydrogenated and refined for use in the manufacture of margarine, salad and cooking oils, and some vegetable shortenings.

[9]Copra Refining, *Chem. Met. Eng.* 52 (2) 148 (1944) (pictured flowchart).

Inedible grades of the oil result from additional hot expressions and are consumed by soapmakers.

Tung oil. Tung or China wood oil is obtained from the fruit of the tung tree, which grows extensively in China. Since 1923, large-scale planting has been carried out in Florida, and tung oil production has become one of the prime industries of that state. Because of the large demand for fast-drying finishes and the difficulties in obtaining this oil from China, various modifications of other oils (Chap. 24) for drying purposes are employed. This oil dries in one-third the time required by linseed oil. The oil is obtained by expression, and the cake, unfit for stock feeding, is used as fertilizer because of its high nitrogen and phosphorus content.

Castor oil. This well-known oil is obtained from the seeds, or beans, of the castor plant found in most tropical regions. The beans contain 35 to 55% oil and are expressed or solvent-extracted. The finest grade of oil is reserved for medicinal purposes. The lower grades are used in the manufacture of transparent soaps, flypaper, and typewriter ink, and as a motor lubricant. Large quantities of the oil are "sulfonated" to produce the familiar turkey-red oil long employed in dyeing cotton fabrics, particularly with alizarin. Dehydrated castor oil is a very important drying oil as described in Chap. 24. This manufactured product compares quite favorably with tung oil, previously imported.

Safflower oil. Safflower oil is the fastest growing of the edible oils, largely because of its high percentage (68%) of the polyunsaturated fatty acid, linoleic acid. The market is for special foods containing unsaturated fats, such as margarine and salad and cooking oils, to which this oil is particularly adapted by reason of its delicate flavor. It also finds use in paints and varnishes. It grows largely in the low-rainfall states of the Great Plains, usually on land diverted from wheat. Oil-free safflower meal is used for cattle food.

Processing of Oils[10]

REFINING.[11] The usual processing of vegetable oils involves degumming and/or steam refining, adsorptive bleaching, hydrogenation, and deodorization. These steps are usually batch operations, although a few continuous processes are in operation.

The oils are degummed by coagulation with a small amount (0.05%) of concentrated phosphoric acid. In the alkali refining methods, the free fatty acids are neutralized with an excess of 0.1% sodium hydroxide solution and the mixture heated to about 75°C to break any emulsions formed. The gums and soaps are removed by centrifugation, and the fatty acids are recovered by acidulation. Steam refining involves degumming, bleaching if necessary, and treatment with sparging steam under high vacuum so that the fatty acids are removed by distillation.

BLEACHING. Bleaching is accomplished by the use of adsorptive bentonite clays for edible oils, and alternatively by chemical reactions for nonedible ones. The bleached oil, if it is to be used for salad oil, is then subjected to a *winterizing* treatment which removes any materials that will solidify out at refrigerator temperatures. This is accomplished by cooling to about 5°C and filtering out any solidified material.

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[10]Gillies, *Shortenings, Margarines, and Food Oils*, Noyes, Park Ridge, N.J., 1974; Erickson, et al., *Handbook of Soy Oil Processing and Utilization*, Am. Oil Chem. Soc., 1980; ECT, 3d ed., vol. 9, 1980, pp. 795–831; Food Plant of the Future, *Food Eng.* 54 (3) 61 (1982).

[11]Wiederman, Degumming, Refining and Bleaching Soybean Oil, *J. Am. Oil Chem. Soc.* 59 (3) 159 (1981).

HYDROGENATION.[12] Hydrogenation or hardening, as applied to fats and oils, may be defined as the conversion of various unsaturated radicals of fatty glycerides into more highly or completely saturated glycerides by the addition of hydrogen in the presence of a catalyst. Various fats and oils, such as soybean, cottonseed, fish, whale, and peanut, are converted by partial hydrogenation into fats of a composition more suitable for shortenings, margarine, and other edible purposes, as well as for soapmaking and numerous other industrial uses. The object of the hydrogenation is not only to raise the melting point but to greatly improve the keeping qualities, taste, and odor for many oils. It is frequently accompanied by isomerization with a significant increase in melting point, caused, for example, by oleic (cis) isomerizing to elaidic (trans) acid. As the reaction itself is exothermic, the chief energy requirements are in the production of hydrogen, warming of the oil, pumping, and filtering. The reaction may be generalized:

$$(C_{17}H_{31}COO)_3C_3H_5 + 3H_2 \xrightarrow{Ni} (C_{17}H_{33}COO)_3C_3H_5 \qquad \Delta H = -420.8 \text{ kJ/kg}$$

Manufacture of hydrogenated oils requires hydrogen-generating equipment, catalyst equipment, equipment for refining the oil prior to hydrogenation, a converter for the actual hydrogenation, and equipment for posthydrogenation treatment of the fat. One type of continuous converter is pictured in Fig. 28.6 but usually the process is a batch operation.[13]

The hydrogen needed may be manufactured by a number of methods, but the hydrocarbon-steam process is the most widely used. Since gaseous sulfur compounds (H_2S, SO_2, etc.) are strong catalyst poisons even in trace amounts, as is carbon monoxide, but to a lesser degree, it is essential that the hydrogen be completely free of these poisons, as well as of taste-producing substances. The amount of hydrogen necessary is a function of the degree of reduction of unsaturation required, as measured by the decrease in the iodine number of the oil during hydrogenation. The theoretical quantity needed to reduce the iodine number one unit is about 0.95 m^3 of hydrogen per metric ton of oil. The catalyst[14] used commercially is nickel. It is generally manufactured by the liquid, or wet-reduced, process.

The catalyst and unsaturated oil are introduced into a specially designed tall, cylindrical closed vessel equipped for accurate temperature control. The charge is heated as quickly as possible to as high as 240°C, but 190°C is a more common temperature. Normal operating pressures are 200 to 700 kPa gage. At about 150°C the nickel formate begins the reduction:

$$Ni(HCOO)_2 \cdot 2H_2O \rightarrow Ni + 2CO_2 + H_2 + 2H_2O$$

The charge is held at the maximum temperature for about 1 h and then cooled. During the reduction and cooling period, hydrogen is bubbled through the oil solely to sweep decomposition products from the oil. Upon completion of the reduction, the charge may be pumped directly to the converter or formed into blocks, flakes, or granules for later use.

The degree of hydrogenation is followed and controlled by refractometer readings to indicate the physical properties (saturation and melting point). The catalyst is filtered off and reused. As the hydrogenation is exothermic, the heat must be removed by an interchanger.

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[12]Allen, Hydrogenation, *J. Am. Oil Chem. Soc.* 58 (3) 166 (1981); Albright, Theory and Chemistry for the Hydrogenation of Fatty Oils, *Chem. Eng.* 74 (19) 197 (1967); Commercial Processes for Hydrogenating Fatty Oils, *Chem. Eng.* 74 (21) 249 (1967).

[13]See Chap. 7 for details of these various processes.

[14]Burke, Catalysts, *Chem. Week* 111 (19) 35 (1972).

Selective, or directed, hydrogenation can also be used, wherein polyunsaturated fatty acids can be largely converted to monounsaturated acids before there is significant conversion of the monounsaturated fatty acids to saturated fatty acids. Also, conditions can be changed to permit hydrogenation of both mono- and polyunsaturated fatty acids simultaneously.

DEODORIZATION. Deodorization is accomplished by blowing superheated steam through the oil (if hydrogenated, while it is still hot and in the liquid stage) under a high vacuum of 138 to 800 Pa and 210 to 275°C. This removes most of the odor-causing compounds and also destroys many of the color-producing pigments present. Final packaging is often done under a nitrogen atmosphere to prevent any deleterious oxidation.[15]

ANIMAL FATS AND OILS

Much chemical processing, started early by hydrogenation and now intensified by interesterification and isomerization, has improved the quality of animal fats and oils.

Neat's-foot oil. The skin, bones, and feet of cattle (exclusive of the hoofs) are cooked or rendered in water for 10 h to separate the fat. This is skimmed off the top of the water and, after filtering through cloth, heated in a kettle to 121°C for several hours. The kettle is cooled, and the contents are settled; the oil is then drawn off, filtered through flannel bags, and sent to the refinery. Here the oil is *grained,* which requires about 2 weeks at 1°C. The product is pressed once, yielding pure neat's-foot oil. The stearin from the first pressing is re-pressed to yield a second grade oil. The pure variety is used for oiling watches and other fine machinery, and the latter in the textile and leather industries. The stearin from the second pressing is consumed in soap manufacture.

Whale oil. This oil is now obtained from modern floating factory ships which catch, butcher, and process the mammals at the scene of the catch. To prepare the oil, the blubber is stripped from the flesh and boiled in open digesters. The finest grade of oil separates first. It is practically odorless, very pale in color, and contains very little free fatty acid. Upon continued boiling, a second grade is obtained and, if the residue from this operation is cooked under pressure, a third grade is made available. All grades are centrifuged to clarify and dry them further before they are placed in storage. The oils obtained are used in the manufacture of lard substitutes and in soapmaking.[16] Both fish and whale oil contain unsaturated fatty acids of 14 to 20 carbon atoms, and as many as six double bonds.

Cod-liver oil. This oil, whose value was known long before the discovery of vitamins, was originally prepared by storing fish in barrels and allowing them to rot until the oil floated to the top. It is now rendered fresh by live steam cooking of cod and halibut livers (and other parts) until a white scum floats to the top. This usually requires about 30 min, after which the mass is settled for 5 min, decanted, and strained. The oil desired for medicinal purposes is filtered, bleached, and winterized. It is rich in vitamins A and D. Lower grades are employed in leather dressing and for poultry feed.

Shark-liver oil. Recent investigations have shown that the oil obtained from the liver of the shark *Galeorhinus zyopterus* contains more vitamins A and D than cod- or halibut-liver

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[15]Gavin, Deodorization and Finished Oil Handling, *J. Am. Oil Chem. Soc.* 59 (3) 175 (1981).

[16]Industrial Use of Whale Oil, *CHEMTECH* 6 (5) 322 (1976).

oil. In 1950, vitamin A was commercially synthesized,[17] and this process has made a sizable dent in the market formerly held by fish-liver oils. This 12-step synthesis process is based on citral, formaldehyde, and acetic acid as raw materials. See Vitamins, Chap. 6.

Fish oils. Fresh menhaden,[18] sardine, and salmon are cooked whole by steaming for a short period and pressed. The oil is settled (or centrifuged) and winterized. The remainder of the fish is dried, pulverized, and sold as meal for feed. Each fish contains, on the average, 20% oil by weight. The oils are consumed in paints, as lubricants, and in leather and soft-soap manufacture, and when sulfonated yield a variety of turkey-red oil.

The tremendous quantities of *butter* and *tallow* produced for food in the United States are shown in Fig. 2.1. Tallow is rendered similarly to lard, and butter fat is obtained by centrifugal separators.

Lard. Lard and lard oil are the most important animal fats and are produced by the rendering of hog fat. Lard oil is the most important of the animal oils and is expressed from white grease, an inedible lard. Lard has been fundamentally upgraded by modern chemical conversions, interesterification and isomerization, which are discussed later.

Processing

ISOMERIZATION REACTIONS. In addition to the formation of more saturated compounds during hydrogenation (Figs. 2.5 and 2.6), the reaction may be accompanied by the formation of isomeric unsaturated fatty acids. These may be positional isomers resulting from the migration of double bonds, or geometric (spatial) isomers resulting from the conversion of naturally occurring cis forms to trans forms. These isomers are of considerable interest, chiefly because of their different physical properties. There is also evidence that the rate of hydrogenation of the different isomers varies, so that their presence affects the overall reaction rate and final composition.[19] One explanation of isomerization is based on the half-hydrogenation–dehydrogenation sequence. During hydrogenation a hydrogen atom can add to either end of the double bond and form a free-radical center, probably still attached to the catalyst. This free-radical center is quite unstable, and if a catalyst is only partially covered with hydrogen, a hydrogen atom may be eliminated from a carbon next to the free-radical center, re-forming the double bond. In this way either a positional isomer is formed or the bond in the initial position is regenerated. Since the formation of a free-radical center allows free rotation, the new unsaturated compound is able to be formed in a cis or trans configuration, according to the thermodynamic stability of each form. Experimental evidence suggests a *trans*-oleic (elaidic)/*cis*-oleic equilibrium ratio of at least 2:1.[20]

To summarize: "The food fat processor can purify to a high degree the natural crude oils. He can change the character of the side chain fatty acids by hydrogenation, and change their relative positions in the triglyceride randomly or controllably by interesterification. He can create solids *in situ*, add them or remove them, and have them assume a stiffening or non-stiffening character. With such flexibility he is providing the public with a variety of palatable and nutritious foods; and if the need arises for fats with special nutritional properties, he has the means to produce them."[21]

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[17]O'Connor, Synthetic Vitamin A, *Chem. Eng.* 57 (4) 146 (1950).

[18]Stansby, *Fish Oils*, Avi, Westport, Conn., 1967.

[19]Allen and Kiess, *J. Am. Oil Chem. Soc.* 33 355 (1956).

[20]For details see James, *Homogeneous Hydrogen*, Wiley-Interscience, New York, 1975.

[21]Sanders, Processing of Food Fats, *Food Technol.* 13 (1) 41 (1959).

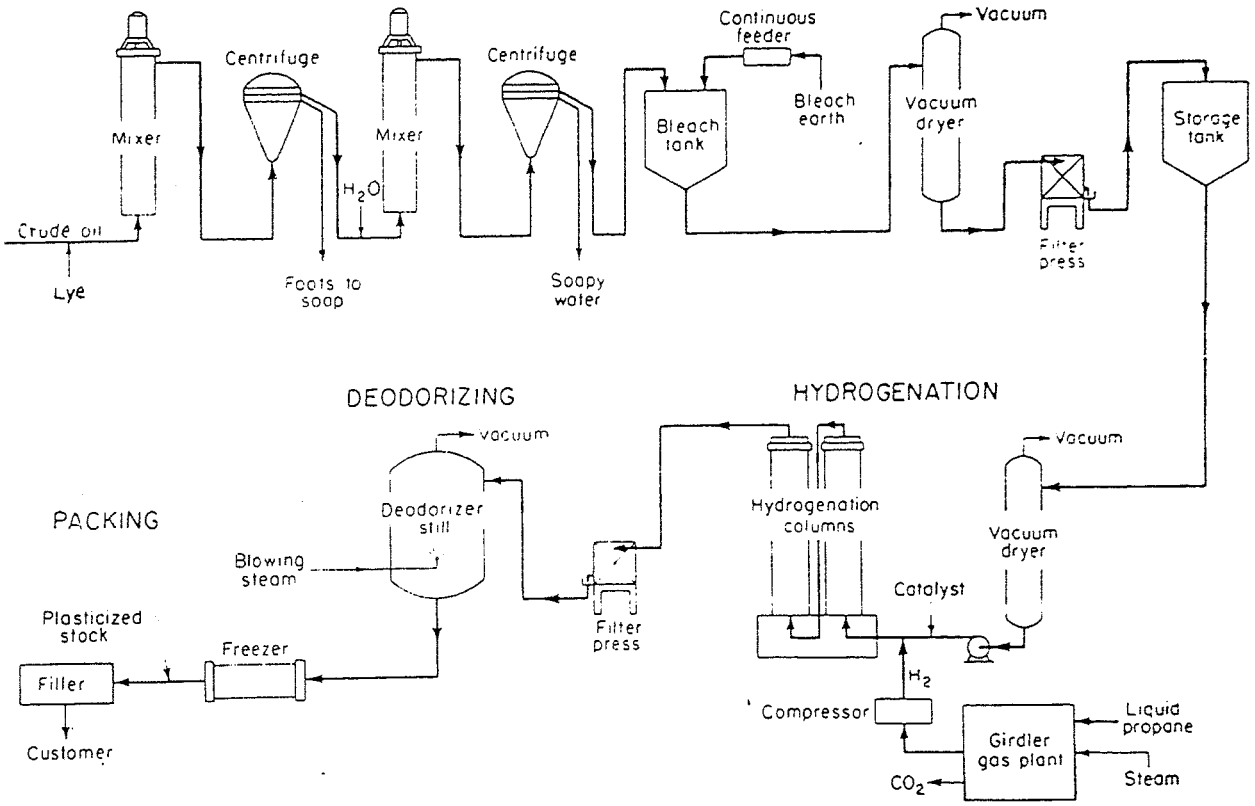


Fig. 2.5. Flowchart for continuous processing of edible oils, either vegetable or animal, including refining, bleaching, hydrogenation, and deodorizing. *(Procter & Gamble Co.)*

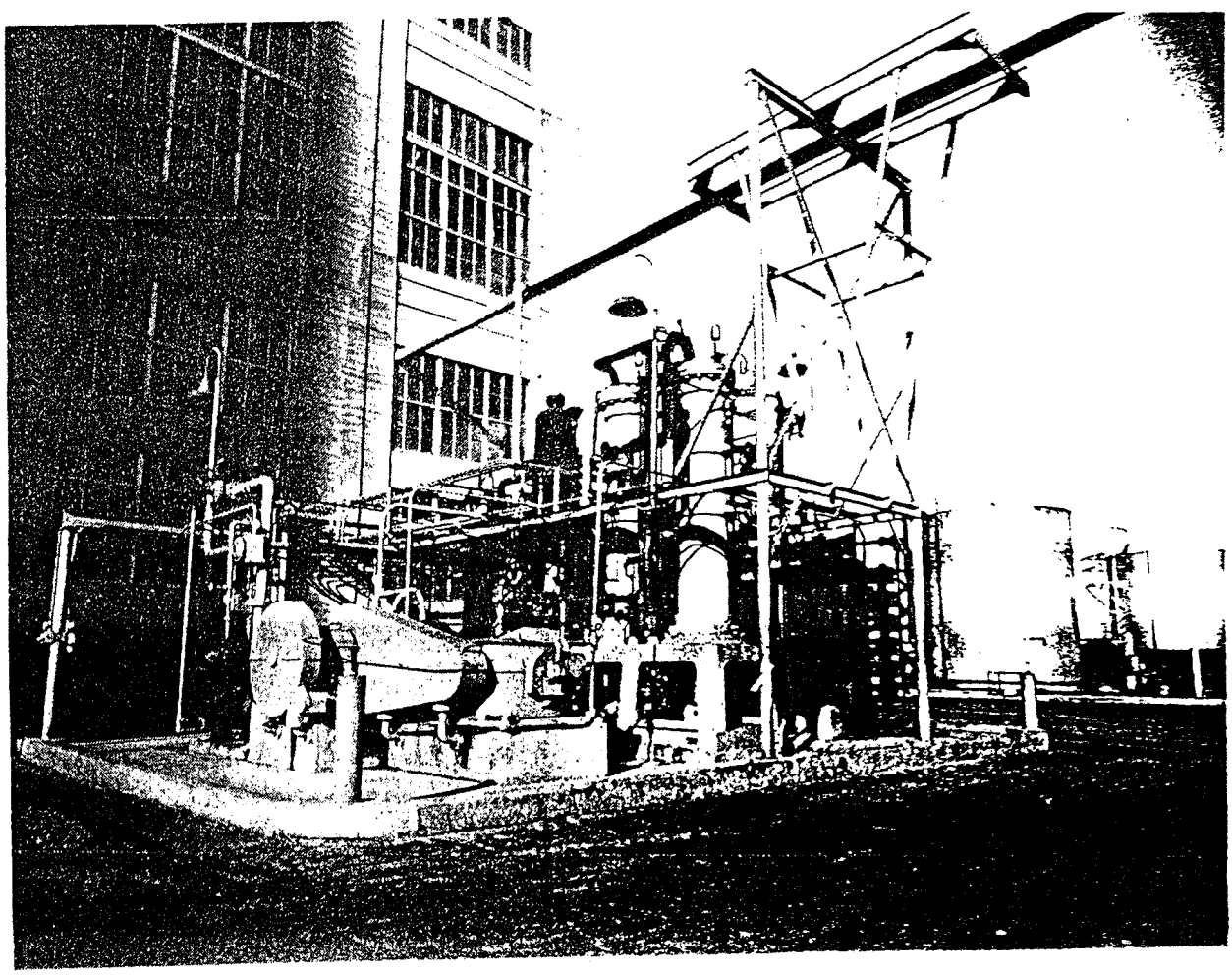


Fig. 2.6. Continuous hydrogenation unit. *(Procter & Gamble Co.)*

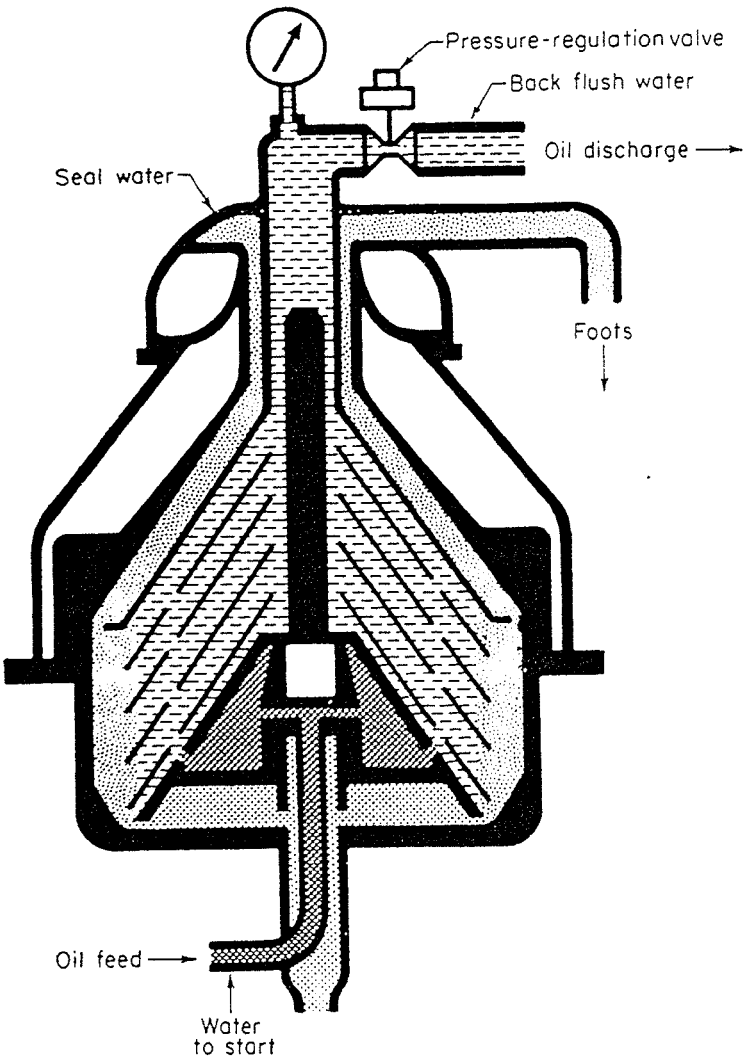


Fig. 2.7. Continuous separating centrifuge as used in the fatty-oil industry. *(Procter & Gamble Co.)*

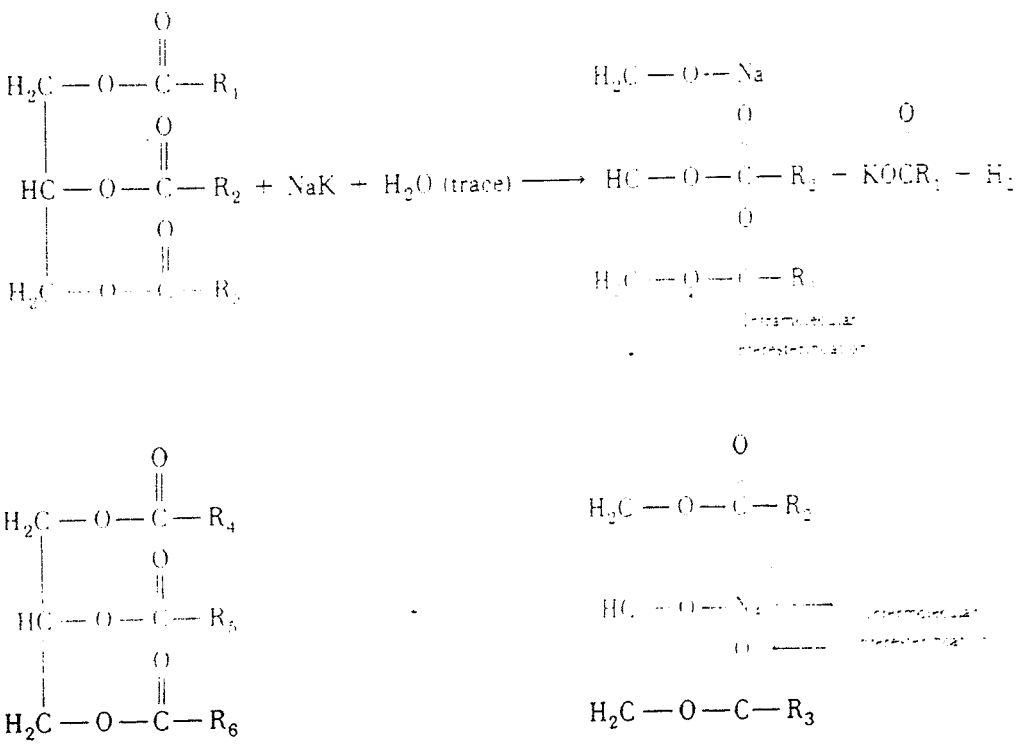
INTERESTERIFICATION. An advance in fat chemistry, which affected the overall amount of crude fats used in shortening manufacture, was the laboratory perfection and large-scale production of shortenings containing lard processed by random and directed interesterification.[22] For many years the blending of lard into good shortening was blocked by certain undesirable inherent characteristics of the lard. Lard has a grainy, translucent appearance and a short plastic range, or range of temperature, over which the fat is of good workability—neither too firm nor too soft. Graininess and short plastic range, however, require a chemical rearrangement of the lard fat glycerides for use in high-grade shortening. Graininess is due to the occurrence of a much greater than random proportion of disaturated triglyceride molecules containing stearic, palmitic, and unsaturated fatty acid chains. About 26 percent of lard triglycerides have this structure. The predominance of one particular type of triglyceride promotes the deposition of this fraction in large crystals over a short period of time. However, if lard is thoroughly dried and heated to 80°C for about 30 min with an alkaline catalyst

[22]Courtesy of Going, Procter & Gamble Co.; Hawley and Holman, Directed Interesterification as a New Processing Tool for Lard, *J. Am. Oil Chem. Soc.* 33 29 (1956); Placek and Holman, *Ind. Eng. Chem.* 49 162 (1957).

(sodium methoxide or Na-K alloy), the side chains will migrate among the glyceryl residues and, within minutes under the right conditions, will reach a random distribution. Neutralization of the catalyst stops the reaction. In such a randomizing process, the particular undesirable disaturated triglyceride structure is found to drop from 26 to about 3½%. Thus, by *randomizing*, the graininess of the lard is counteracted. Several commercial lard-based shortenings are produced[23] from such randomized lard.

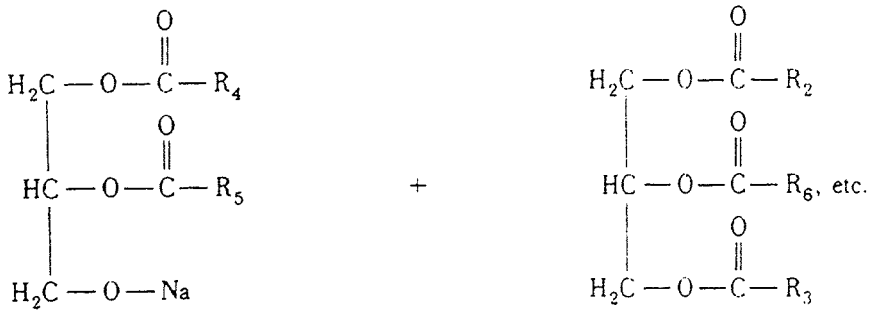
Extending the plastic range of lard requires further processing. Most of the solids in lard or randomized lard are disaturated glycerides, which give shortening little or no heat resistance, since they melt at higher atmospheric temperatures. Ideally, a process is desired which uses disaturates to produce trisaturates and triunsaturates that do not change their physical state over the ambient temperature range but remain, respectively, solid and liquid. This has been found in what is termed *directed interesterification*.[24] If, in the presence of an active rearrangement catalyst, the randomized lard mass is chilled, fat solids in transient existence will irreversibly precipitate out. In cooling from the melt, the first solids to separate will be trisaturates. If the temperature is held slightly below the melting point of the trisaturates they will continue to separate so long as the constantly rearranging melt continues to rearrange saturated fatty acids into trisaturates in a futile attempt to reach equilibrium. Therefore the lard composition changes with time, and trisaturates and triunsaturates increase at the expense of mono- and disaturates. When the catalyst is neutralized, the composition remains frozen in the new form.

Interesterification reactions



[23]Going, U.S. Patent 2,309,949 (1943); Van der Wal et al., U.S. Patent 2,571,315 (1951) Holman et al., U.S. Patent 2,738,278 (1956).

[24]Eckey, U.S. Patents 2,422,531 and 2,442,532 (1948); Hawley, U.S. Patent 2,733,251 (1956); Holman et al., U.S. Patents 2,875,066 and 2,875,067 (1959).



These reactions proceed to a statistically random equilibrium of fatty acid combinations in the triglyceride molecules. In directed interesterification, a molecule crystallizes when its three fatty acids are saturated.

The flowchart in Fig. 2.8 presents the process steps in rearrangement. Dried lard is catalyzed with a sodium-potassium alloy, mixed, chilled in two stages, and crystallized. The end point is controlled by the cloud point. The reaction mass is neutralized and heated to separate the fat phase from the soap phase formed during neutralization of the catalyst.

WAXES[25]

There are animal, vegetable, mineral, and synthetic waxes, depending upon the source. Animal waxes are secreted as protective coatings by certain insects. Vegetable waxes are found as coatings on leaves, stems, flowers, and seeds. Mineral waxes are paraffin waxes obtained from petroleum, and such waxes as are yielded by coal, peat, and lignite. Mineral waxes from petroleum are not true waxes (esters) but are so classified because of their physical characteristics.

BEESWAX. This is probably the best-known wax. It is made from honeycombs by solvent extraction, expression, or boiling in water. Many church candles contain more than 50% of this wax.

CARNAUBA WAX. This wax is obtained from the carnauba palm, which grows in Brazil. The leaves are cut, dried for 3 days, and sent to the beater house. The drying loosens the wax, which can be easily beaten from the slashed leaf, and it falls to the floor where it is gathered at the end of the day and melted. Less than 1 L of molten wax is obtained from 19 L of powdered wax. This is filtered through cheesecloth, allowed to harden, and sold. A palm tree produces about 90 g of wax per year. The product is used as a constituent of floor, automobile, and furniture polishes, and in carbon paper, candles, and certain molded products.

SPERMACETI. The oil removed from the head cavity, and parts of the blubber of the sperm whale is in reality a wax because of its chemical composition. Spermaceti is important for lubrication. The head oil, upon chilling and setting, is a solid wax. This constitutes about 11% of the original oil and is largely cetyl palmitate. It is melted, treated with a hot, dilute caustic soda solution, washed with water, and run into molds to solidify. It is translucent, odorless, and tasteless and is used chiefly as a base for ointments. By methylating sperm oil, Archer-Daniels-Midland has obtained a low surface tension (0.0017 to 0.0018 N/m) lubricant.

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[25]Bennett, *Industrial Waxes*, 2d ed., Chem. Publ. Co., New York, 1975.

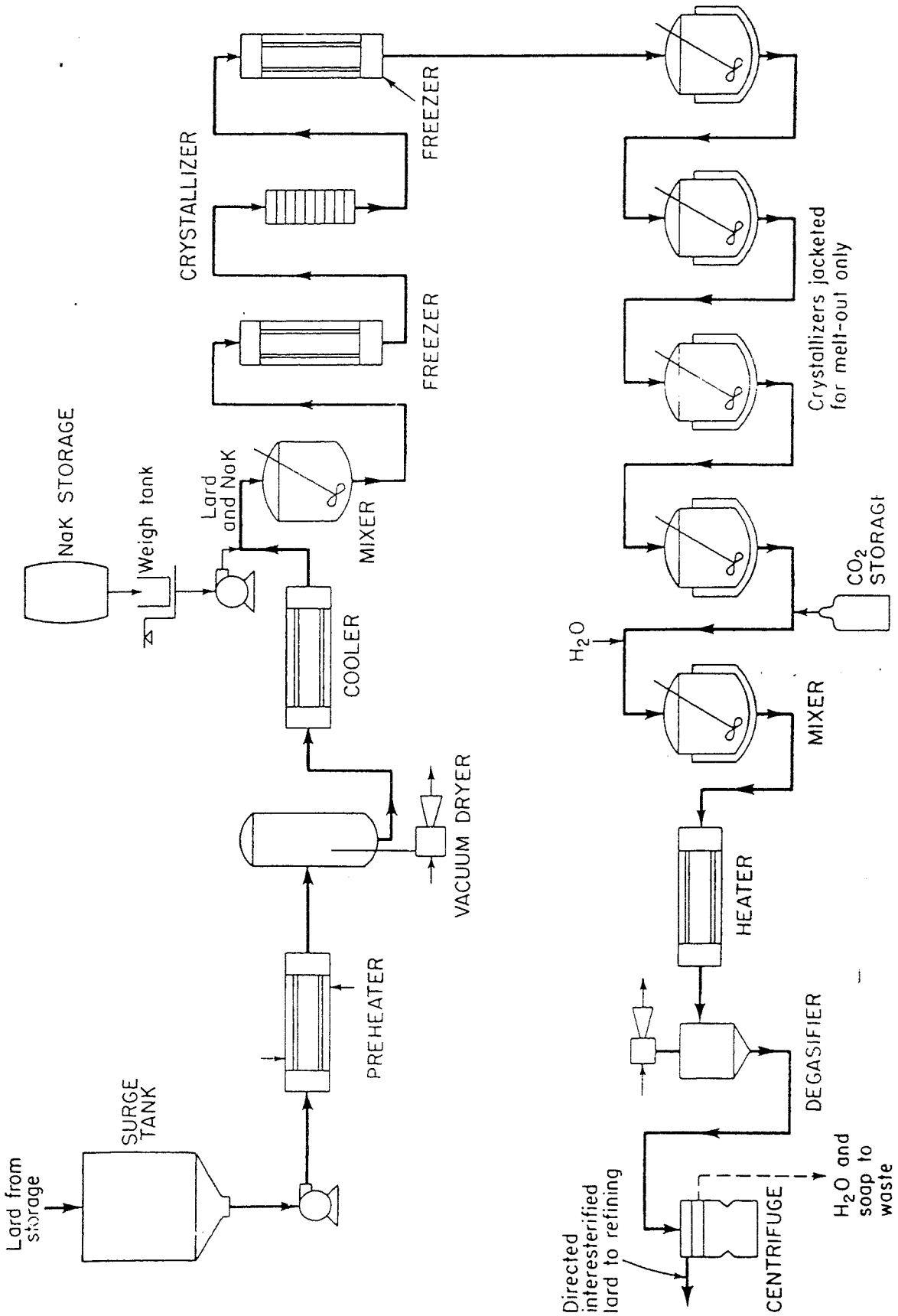

Fig. 2.8. Flowchart for continuous production of lard by direction interesterification. (*Procter & Gamble Co.*)

OZOCERITE. This is the name given to certain naturally occurring mineral waxes. The ozocerite known commercially is a particular earth wax mined in eastern Europe, but important similar waxes are mined elsewhere. One variety, mined in Utah, is known as Utahwax or Utah ozocerite. It can be substituted to a great extent for the other and is chiefly employed for electrical insulations, waterproofing, and impregnating.

PARAFFIN WAX. This wax is concentrated in certain lubricating-oil fractions as a result of distillation and is separated by chilling and filter-pressing (Chap. 37). Extraction of lube oil fractions with, e.g., a mixture of methyl ethyl ketone and benzene, followed by distillation into narrow-boiling fractions yields microcrystalline waxes.

MONTAN WAX. The name montan wax generally applies to the wax obtained from a bituminous wax solvent-extracted from bituminous lignite or shale, but a similar wax may be obtained from peat or brown coal. Its important applications include electrical insulations. polishes, and pastes.

CANDELILLA WAX. This is the third most important U.S. wax in tonnage and is made by boiling the stems of a plant common in Mexico and the southwestern United States with a water-sulfuric acid mixture and skimming off the wax which floats on the liquid. Another method of obtaining this wax is by extracting the stems with hexane and recovering the wax by distillation of the solvent.[26]

SYNTHETIC WAXES. Various materials are used to make synthetic waxes. Carbowaxes are high molecular weight polyethylene glycols. They are useful as wax emulsifiers, as well as being waxy themselves. Higher aliphatic alcohols are used as emulsified wax substitutes. Other synthetic waxes are produced from fatty acids and amines, and chlorinated paraffin waxes.

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[26] *Chem. Eng.* 87 (10) 85 (1980).

Chapter 3

Soap and Detergents

The washing industry, usually known as the soap industry, has roots over 2000 years in the past, a soap factory having been found in the Pompeii excavations. However, among the many chemical process industries, none has experienced such a fundamental change in chemical raw materials as have the washing industries. It has been generally accepted that the per capita use of toilet soap is a reliable guide to the standard of living for any country.

HISTORICAL. Soap itself was never actually "discovered," but instead gradually evolved from crude mixtures of alkaline and fatty materials. Pliny the Elder described the manufacture of both hard and soft soap in the first century, but it was not until the thirteenth century that soap was produced in sufficient quantities to call it an industry. Up to the early 1800s soap was believed to be a mechanical mixture of fat and alkali; then Chevreul, a French chemist, showed that soap formation was actually a chemical reaction. Domeier completed his research on the recovery of glycerin from saponification mixtures in this period. Until Leblanc's important discovery producing lower-priced sodium carbonate from sodium chloride, the alkali required was obtained by the crude leaching of wood ashes or from the evaporation of naturally occurring alkaline waters, e.g., the Nile River.

The raw material shortages of World War I led the Germans to develop "synthetic soaps" or detergents. These were composed of short-chain alkyl naphthalene sulfonates, which were good wetting agents but only fair in detergent action. This sparked the interest worldwide in developing detergents, and new developments are continuing to the present time. From the original short-chain compounds the development has progressed through long chain alcohol sulfates in the 1920s and 1930s, through alkyl-aryl long chain sulfonates in the 1940s, to branched chain compounds in the 1950s and 1960s. During the 1960s the requirement of biodegradability became important and caused the return to linear long chains, because only the linear chains can be easily biodegraded.

USES AND ECONOMICS.[1] In 1981 the total value of surfactant and soap shipments was $10,701 million. Of this, the value of household soap shipments was about $1300 million and for household detergent products, $4000 million. Out of a total demand of 3200 kt, soap represented 39 percent with a demand of 540 kt and detergents accounted for 840 kt.[1a] Indus-

[1] *U.S. Industrial Outlook, 1982,* U.S. Dept. of Commerce; Layman, Surfactants—A Mature Market with Potential, *Chem. Eng. News* 60 (2) 13 (1982); Moffet and von Hennig, Detergent Activities, *Soap Cosmet. Chem. Spec.* 57 (9) 29 (1981); Piellisch, Stronger Than Dirt: The Battle of the Detergent Chemicals, *Chem. Bus.* June 29, 1981, p. 33.

[1a] t = 1000 kg; kt = 10^6 kg.

trial uses accounted for the difference. Figure 3.1 and Tables 3.1 and 3.3 show the gradual replacement of soap by detergents in the household market.

Laundry products, toilet soaps, shampoos, dishwashing products, and cleaning products are the chief household uses of these materials. Industrial uses include cleaning compounds, specialty surfactants for hospital germicides, fabric conditioners, emulsifiers for cosmetics, flowing and wetting agents for agricultural chemicals, and rubber processing aids. A potentially large use is for enhanced oil recovery from presently "worked-out" oil wells.

DETERGENTS[2]

Detergents differ from soap in their action in hard water. Soaps form insoluble compounds with the calcium and magnesium ions present in hard water. These insoluble compounds precipitate out and reduce foaming and cleaning action. Detergents may react with the hard water ions, but the resulting products are either soluble or remain colloidally dispersed in the water. Table 3.2 illustrates the differences between soaps and detergents in composition and manufacture. Table 3.3 shows the consumption of surfactants in detergents.

Detergents have been divided into four main groups: anionic, cationic, nonionic, and amphoteric. The largest group consists of the anionics which are usually the sodium salts of

[2]Scientifically, the term detergent covers both soap and synthetic detergents, or "syndets," but it is widely used to indicate synthetic cleaning compounds, as distinguished from soap. It is so used in this book. The U.S. Tariff Commission reports on detergents under the name surface-active agents or surfactants under the broader class of synthetic organic chemicals.

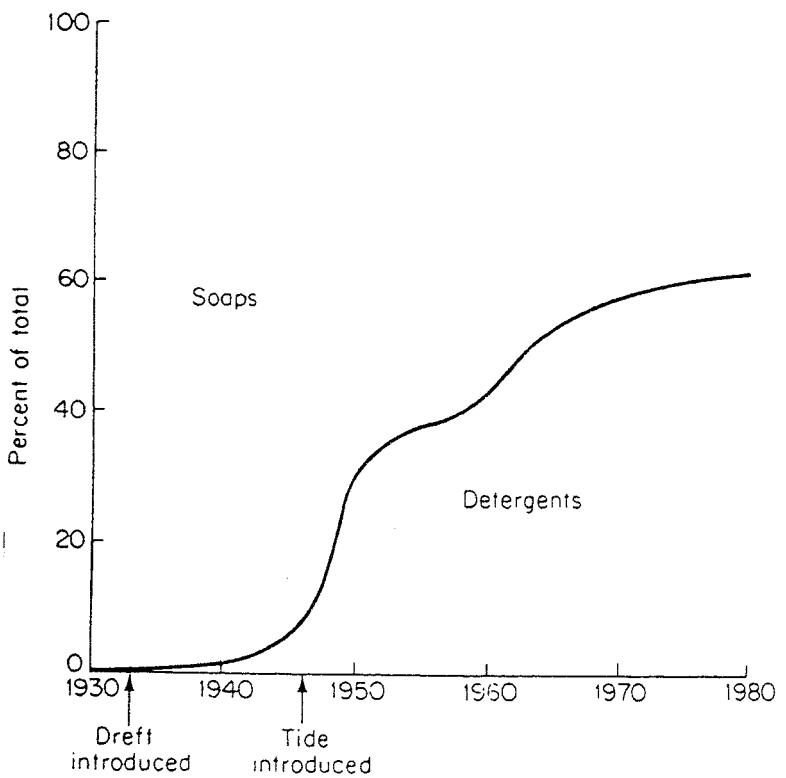


Fig. 3.1. Relative production of detergents and soap.

Table 3.1 Production and Sales of Soaps and Surfactants

	Soap		Surfactants		Total	
	10^6\$	kt	10^6\$	kt	10^6\$	kt
1940	313	1455	7	13	320	1468
1945	527	1717	35	68	562	1785
1950	540	1308	294	655	834	1963
1960	376	558	953	1789	1329	2347
1970	427	567	1379	2565	1806	3132
1980	1030	545	8430	2663	9460	3208

SOURCE: CPI 4, chap. 29; *U.S. Industrial Outlook, 1982*, U.S. Dept of Commerce.

an organic sulfate or sulfonate. Detergents can be formulated to produce a product of the desired characteristics ranging from maximum cleaning power, maximum cleaning unit cost, to maximum biodegradability. Usually commercial products are a compromise of the various desirable properties.

Soil removal is accomplished by wetting, emulsifying, dispersing, and/or solubilizing the soil by the cleaning agent. Detergent molecules can aggregate in water into spherical clusters called micelles. The hydrocarbon parts of the molecules gather together on the inside of the micelle and the polar groups are on the outside. Oil-soluble water-insoluble compounds, such as dyes, are often dissolved into the center of the micelle attracted by the hydrocarbon groups. This process is known as solubilization.[3]

Detergents and soaps have water-attracting (hydrophilic) groups on one end of the molecule and water-repelling (hydrophobic) groups on the other. These special properties are used in soil removal.

During the 1960s and 1970s, the composition of detergents underwent rapid changes because of environmental considerations.[4] Evidence indicated that phosphates from deter-

[3]*McGraw-Hill Encyclopedia of Science and Technology*, 5th ed., vol. 12, McGraw-Hill, New York, 1982, p. 488.

[4]For Detergent Producers, the Question Is Which? *Chem. Week* 129 (4) 44 (1980).

Table 3.2 Soaps and Detergents

To Make Synthetic Detergents
- Alkylbenzene + oleum → alkylbenzene sulfonate
- Tallow fatty alcohol + oleum → fatty alcohol sulfate
- Sulfonate + sulfate + NaOH → sodium salts
- Sodium salts + builders, etc. → detergents

To Make Soap
- Tallow + hydrolysis (splitting fats) → tallow fatty acid
- Tallow fatty acid + NaOH → sodium salt of fatty acid
- Salt of fatty acid + builder, etc. → soap

Table 3.3 Detergent Consumption of Surfactants (in metric kilotons)

	Powders	Liquids
Anionics		
Alkylbenzene sulfonate	145	43
Alcohol ethoxy sulfates	45	Small
Alcohol sulfates	23	—
Nonionics		
Alcohol ethoxylates	45	41
Alkyl phenol ethoxylates	5	5
Amines, amine oxides	5	5

SOURCE: *Chem. Week* 127 (20) 33 (1980).

gents may contribute to the eutrophication of lakes, so the use of phosphates in detergents was banned in some areas of the country. Many different substitutes were formulated into detergents, but some of these were found to be unsafe and were then banned. The position taken by the detergent industry has been that phosphates in wastewater can be removed by special treatment in sewage plants and, in view of the proved lack of toxicity of phosphates, their replacement may not be the most desirable solution. The soap and detergent industry and its suppliers face an enormous task in testing new materials for all possible effects on the environment, and extensive research will be needed before this complex problem can be solved.

Raw Materials

A large volume of active organic compounds, or surfactants,[5] for both detergents and soap are manufactured in final form by soap and detergent companies. Examples are linear alkylbenzene sulfonate (LAS) and fatty alcohol sulfate, which these companies manufacture in hundreds of millions of pounds. The same is true for fatty acids, the basic materials for soaps. Most of the inorganic materials, such as oleum, caustic soda, and various sodium phosphates and a large number of additives, the last mentioned amounting to 3% or less of the total product weight are purchased.

SURFACTANTS. These embrace "any compound that affects (usually reduces) surface tension when dissolved in water or water solutions, or which similarly affects interfacial tension between two liquids. Soap is such a material, but the term is most frequently applied to organic derivatives such as sodium salts of high molecular weight alkyl sulfates or sulfonates."[6] The surfactants of both soap and synthetic detergents perform the primary cleaning and sudsing of the washing action in the same way through the reduction of surface tension. The cleaning process consists of (1) thoroughly wetting the dirt and the surface of the article being washed with the soap or detergent solution, (2) removing the dirt from the surface, and (3) maintaining the dirt in a stable solution or suspension (detergentcy). In wash water, soaps or detergents increase the wetting ability of the water so that it can more easily penetrate the fabrics and reach the soil. Then soil removal begins. Each molecule of the cleaning solution may be considered a long chain. One end of the chain is hydrophilic (water-loving); the other is hydrophobic (water-hating, or soil-loving). The soil-loving ends of some of these molecules are attracted to a soil particle and surround it. At the same time the water-loving ends pull the molecules and the soil particles away from the fabric and into the wash water. This is the action which, when combined with the mechanical agitation of the washing machine, enables a soap or detergent to remove soil, suspend it, and keep it from redepositing on clothes.

Classification. In most cases the hydrophobic portion is a hydrocarbon containing 8 to 18 carbon atoms in a straight or slightly branched chain. In certain cases, a benzene ring may replace some of the carbon atoms in the chain, for example, $C_{12}H_{25}-$, $C_9H_{19}\cdot C_6H_4-$. The hydrophilic functional group may vary widely and may be anionic, e.g., $-OSO_4^-$ or SO_3^{2-}; cationic, e.g., $-N(CH_3)_3^+$ or $C_5H_5N^+$; or nonionic, e.g., $-(OCH_2CH_2)_nOH$.

In the anionic class one finds the most used compounds, namely linear alkylbenzene sulfonates from petroleum and alkyl sulfates from animal and vegetable fats (Fig. 3.2). Soap is

[5]Abbreviation for surface-active agents.

[6]Rose, *The Condensed Chemical Dictionary*, 6th ed., Reinhold, New York, 1961.

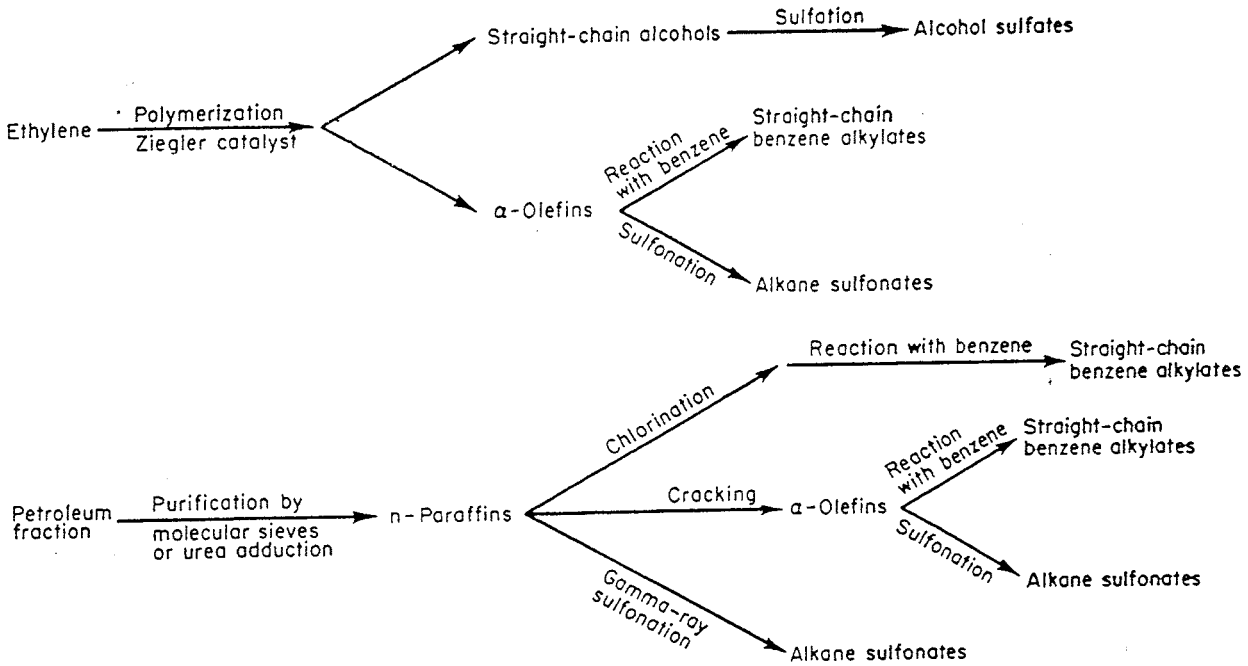
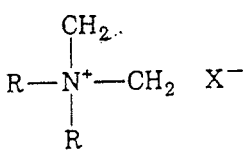
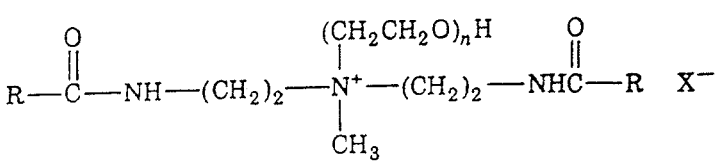


Fig. 3.2. Some possible paths to soft-detergent components. [*Chem. Eng.* 70 *(18)* 25 *(1963).*]

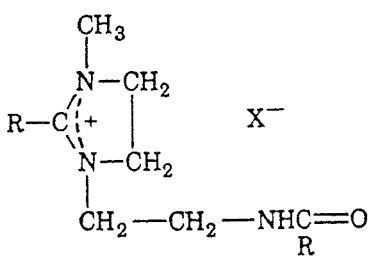
also anionic in character. Quaternary ammonium compounds comprise the cationic class. Three general types are used, mainly for fabric softeners. Type A is a dialkyl dimethyl quaternary ammonium compound



where X^- is either Cl^- or $CH_3SO_4^-$. Type B is a diamido alkoxylated quaternary ammonium compound, where X^- is $CH_3SO_4^-$.



Type C[7] is an amido imidazolinium compound where X^- is $CH_3SO_4^-$.



[7]Williams, How to Choose Cationics for Fabric Softeners, *Soap Cosmet. Chem. Spec.* 58 (8) 28 (1982).

Being generally weak in detergent power, although they have good lubricating, antistatic, and germicidal properties, they are not usually used as household detergents. Anionics and cationics are not compatible with soap.

Ethylene oxide condensates of fatty alcohols illustrate the molecular structure of nonionic surfactants. There are many excellent soil-removing types that are low sudsers and hence are useful in drum-type automatic clothes washers. Nonionics are more effective than anionics in removing soil at the lower temperatures necessary for laundering synthetic fibers. They are also more effective at removing body oils.

Biodegradability.[8] In view of the attention being given to water pollution control and abatement, product-development chemists and chemical engineers have realized that surfactants being developed for use in household and industrial detergents that go down the drain to the sewer must be readily decomposable to inorganic compounds by the microbial action of sewage treatment and in surface streams. This new parameter has been added to the performance, efficiency, and cost factors the detergent industry must consider in developing new products. Some surfactants, like tetrapropylene-derived alkylbenzene sulfonate, degrade slowly, leaving a persistent residue. Others are more readily decomposable by microorganisms and leave practically no persistent residues. The ease with which a surfactant is decomposed by microbial action has been defined as its biodegradability. Tests are being developed and standards are being established for biodegradability. To have broad application, such standards must recognize the breadth of variation in environmental conditions. Materials which may be only partly degraded in inefficient treatment processes can be completely decomposed by more sophisticated biological treatment systems. Methods of testing radiolabeled surfactants of anionic, cationic, and nonionic types and builders have been developed to determine the rate of biodegradation in parts per billion in natural waters and also to determine if threshold concentrations, below which degradation is not observed, exist.[9]

STRAIGHT-CHAIN ALKYLBENZENES. Biodegradable detergents are made primarily from phenyl-substituted *n*-alkanes of 11 to 14 carbon atoms. The straight-chain paraffins or olefins needed are produced from petroleum as shown in Fig. 3.2. In 1981, 233 kt were produced in the United States.

n-Alkanes are separated from kerosene by adsorption using molecular sieves. Branched chain and cyclic alkanes have larger cross-sectional diameters than do the linear molecules, thus making sieve separation possible. The other common method of separation of the normal paraffin compounds from the branched and cyclic ones is by reaction with urea or thiourea. Urea will react with linear chain hydrocarbons having at least seven carbon atoms to give a crystalline adduct which is separable by filtration. No such adduct is formed with the branched chain or cyclic compounds. The adduct can then be decomposed by heating with hot water at 80 to 90°C. Conversely, thiourea will react with the branched chain hydrocarbons but will not form adducts with straight-chain or aromatic ones. The separated *n*-paraffins are converted to benzene alkylates or are cracked to yield α-olefins.

Linear olefins are prepared by dehydrogenation of paraffins, by polymerization of ethylene to α-olefins using an aluminum triethyl catalyst (Ziegler-type catalyst), by cracking paraffin wax, or by dehydrohalogenation of alkyl halides.

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[8]Larson, "Role of Biodegradation Kinetics in Predicting Environmental Fate," in Maki, Dickson, and Cairns (ed.), *Biotransformation and Fate of Chemicals in the Aquatic Environment*, Am. Soc. for Microbiol. Publ., Washington, D.C., 1980.

[9]Larson and Wentler, Biodegradation of Detergent Materials, *Soap Cosmet. Chem. Spec.* 58 (5) 53 (1982).

α-Olefins or alkane halides can be used to alkylate benzene through the Friedel-Crafts reaction, employing hydrofluoric acid or aluminum fluoride as a catalyst.

FATTY ACIDS AND FATTY ALCOHOLS

Economics. Fatty alcohols and fatty acids are mainly consumed in the manufacture of detergents and soaps. Fatty acids, both saturated (e.g., stearic acid) and unsaturated (e.g., oleic), have long been employed in many industries as both free acids, and, more frequently, as salts. Examples are:

Magnesium stearates in face powders.
Calcium or aluminum soaps (insoluble) employed as water repellents in waterproofing textiles and walls.
Triethanolamine oleate in dry cleaning and cosmetics.
Lithium stearate as a component of greases.
Rosin soap consumed as a sizing for paper.

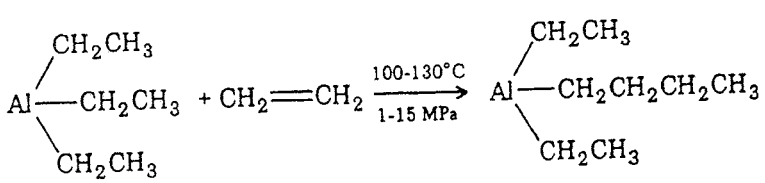
Manufacture of Fatty Acids.[10] Basic raw materials, such as oils and fats, which have been used for a long time (Chap. 2), have, since about 1955, been very extensively supplemented by improved chemical processing and by synthetic petrochemicals. A selection from these processes is given here. Table 3.4 compares three processes for splitting fats that have been used for many years. Figure 3.3 illustrates the high-pressure hydrolysis, catalyzed by zinc oxide, which is used in the soap industry. Fatty acids are drawn off from the distillate receiver for sale or for further conversion to fatty acid salts (calcium, magnesium, zinc, etc.). Several older and less used separation methods for purifying fatty acids are panning and pressing, fractional distillation, and solvent crystallization.

Manufacture of Fatty Alcohols. The Ziegler catalytic procedure for converting α-olefins to fatty alcohols and the methyl ester hydrogenation process are the important methods for preparing fatty alcohols. See also the flowchart in Fig. 3.4 and the text presented under soap for the continuous hydrolysis of fats to furnish fatty acids which may be hydrogenated to fatty alcohols.

The Ziegler[11] procedure is an important one for manufacturing C_{12} to C_{18} α-olefins and fatty even-numbered straight-chain alcohols for detergents. See Fig. 3.4. Gaseous ethylene is converted to higher, linear aluminum trialkyls and α-olefins by the action of aluminum triethyl which takes part in the reactions.

$$CH_2{=}CH_2 + CH_2{=}CH_2 \rightarrow CH_3CH_2CH{=}CH_2$$
$$+ CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2CH_2CH{=}CH_2 \text{ etc.}$$

CHAIN GROWTH REACTION



[10]ECT, 3d ed., vol. 4, 1978, p. 837.

[11]Sittig, *Detergent Manufacturing*, Noyes, Park Ridge, N.J., 1979; ECT, 3d ed., vol. 1, 1978, p. 740.

***Table* 3-4** Tabular Comparison of the Various Fat-Splitting Processes

	Twitchell	Batch autoclave		Continuous Countercurrent*
Temperature, °C	100–105	150–175	240	250
Pressure, MPag		5.2–10.0	2.9–3.1	4.1–4.9
Catalyst	Alkyl-aryl sulfonic acids or cycloaliphatic sulfonic acids, both used with sulfuric acid 0.75–1.25% of the charge	Zinc, calcium, or magnesium oxides, 1–2%	No catalyst	Optional
Time, h	12–48	5–10	2–4	2–3
Operation	Batch	Batch		Continuous
Equipment	Lead-lined, copper-lined, Monel-lined, or wooden tanks	Copper or stainless-steel autoclave		Type 316 stainless tower
Hydrolyzed	85–98% hydrolyzed 5–15% glycerol solution obtained, depending on number of stages and type of fat	85–98% hydrolyzed 10–15% glycerol, depending on number of stages and type of fat		97–99% 10–25% glycerol, dependent on type of fat
Advantages	Low temperature and pressure; adaptable to small scale; low first cost because of relatively simple and inexpensive equipment	Adaptable to small scale; lower first cost for small scale than continuous process; faster than Twitchell		Small floor space; uniform product quality; high yield of acids; high glycerin concentration; low labor cost; more accurate and automatic control; lower annual costs
Disadvantages	Catalyst handling; long reaction time; fat stocks of poor quality must often be acid-refined to avoid catalyst poisoning; high steam consumption; tendency to form dark-colored acids; need more than one stage for good yield and high glycerin concentration; not adaptable to automatic control; high labor cost	High first cost; catalyst handling; longer reaction time than continuous processes; not so adaptable to automatic control as continuous; high labor cost; need more than one stage for good yield and high glycerin concentration		High first cost; high temperature and pressure; greater operating skill

SOURCE: Mostly from Marsel and Allen, Fatty Acid Processing, *Chem. Eng.* 54 (6) 104 (1947). Modified in 1982.
*See Fig. 29.8.

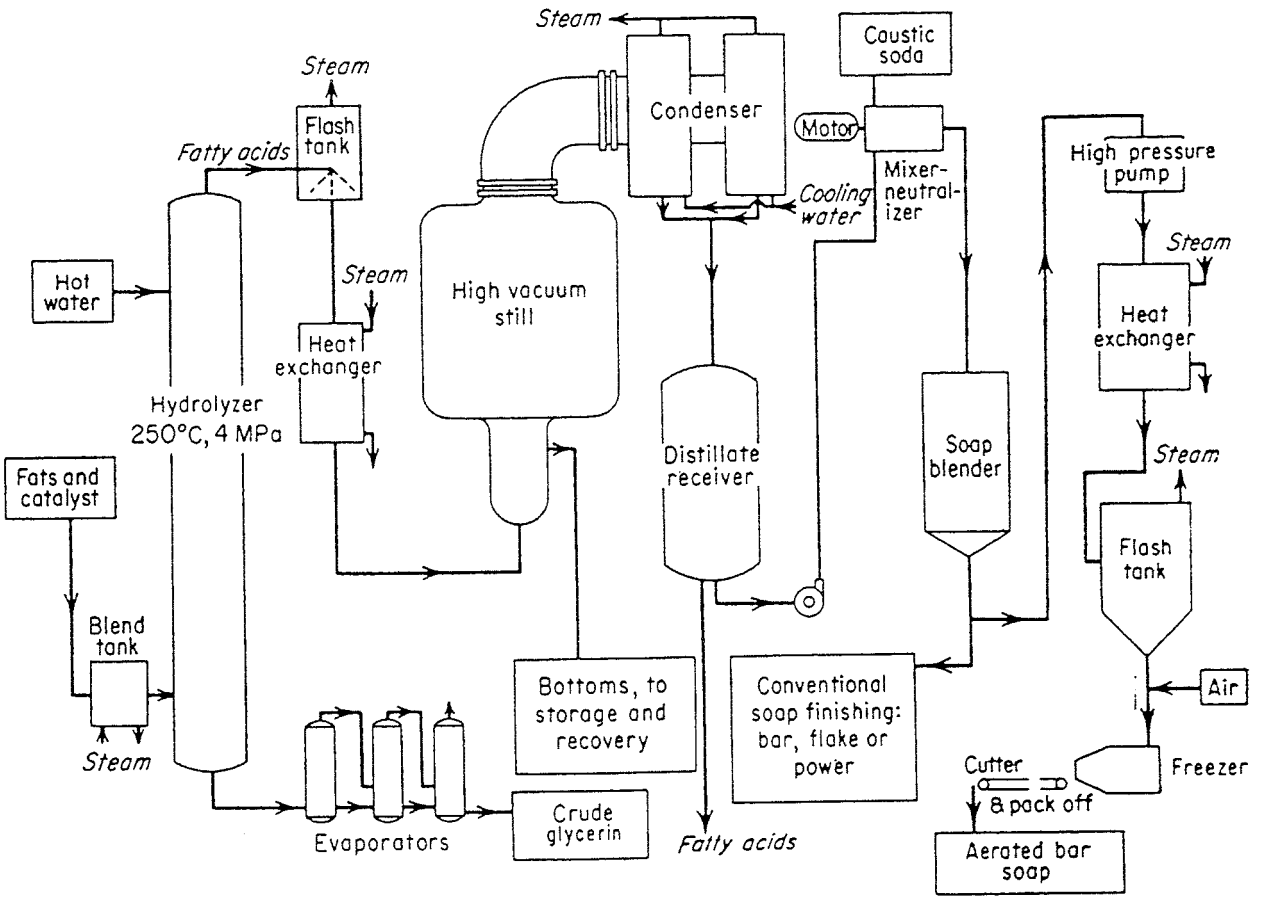


Fig. 3.3. Continuous process for the production of fatty acids and soap. *(Procter & Gamble Co.)*

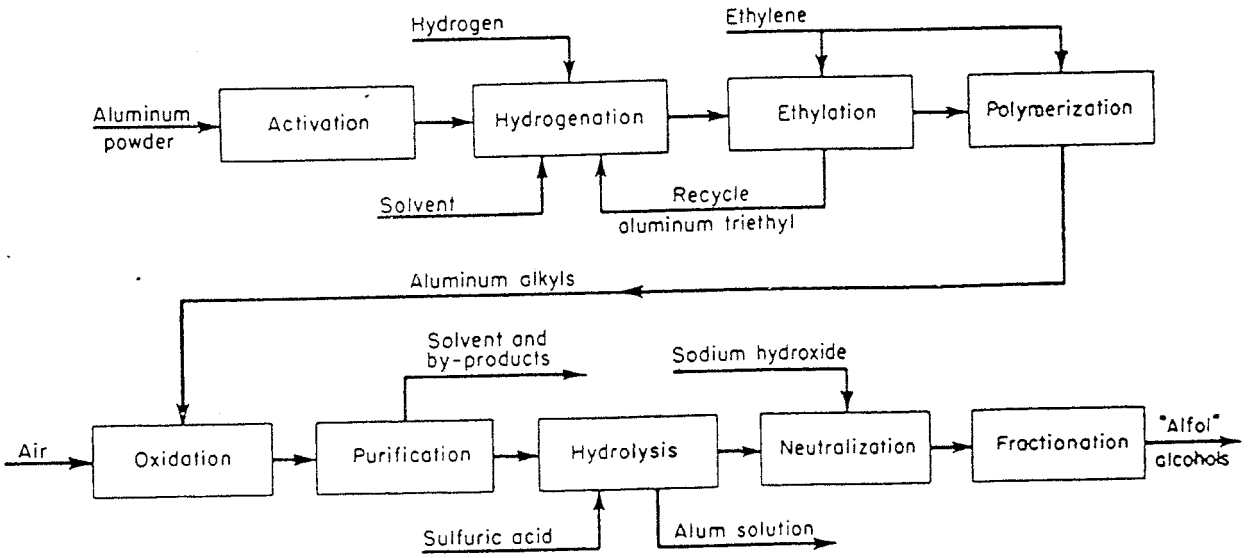
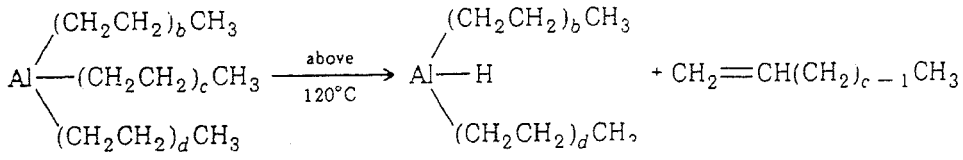


Fig. 3.4. The alfol process. Fatty alcohols made by means of the organometallic route have carbon chain lengths ranging from 6 to 20 carbons. The alfol process used by Conoco commences by reacting aluminum metal, hydrogen, and ethylene, all under high pressure, to produce *aluminum triethyl*. This compound is then polymerized with ethylene to form aluminum alkyls. These are oxidized with air to form aluminum alkoxides. Following purification, the alkoxides are hydrolyzed with 23 to 26% sulfuric acid to produce crude, primary, straight-chain alcohols. These are neutralized with caustic, washed with water, and separated by fractionation. Basic patents covering the process have been licensed. *(DuPont-Conoco.)*

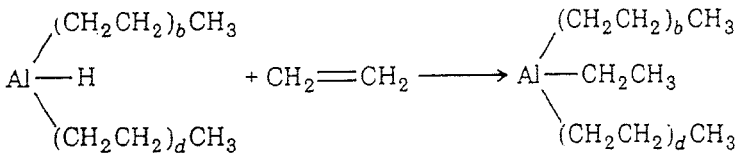
Each ethyl group on the aluminum triethyl can add ethylene to form aluminum trialkyls of 4 to 16 or more carbons per alkyl group.

DISPLACEMENT REACTIONS

Thermal decomposition

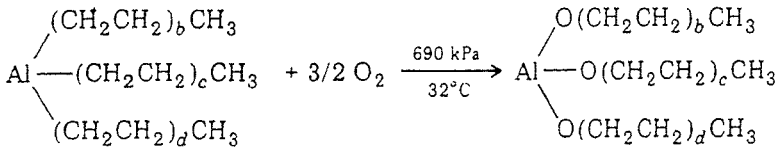


Regeneration of ethyl group



The growth and displacement reactions take place concurrently, but the thermal decomposition reaction is much slower than the regeneration reaction and thus is the rate-determining step for the overall reactions. These reactions take place repeatedly as long as unreacted ethylene is present. They are run in an inert hydrocarbon solvent such as heptane or benzene. In these solvents aluminum "trialkyl" is not pyrophoric at less than 40% concentration. It takes approximately 140 min to build up to a C_{12} average chain length when reacting 5 mol of ethylene for each ⅔ mol of aluminum triethyl The trialkyl aluminum is oxidized to yield an aluminum trialkoxide, which in turn is treated with sulfuric acid to give alkyl or fatty alcohols.

OXIDATION REACTION



ΔH is exothermic, liberating about 2.5 MJ/kg of oxidized alkyl. Its conversion is 98 percent at 32°C in about 2 h.

HYDROLYSIS (ACIDOLYSIS)

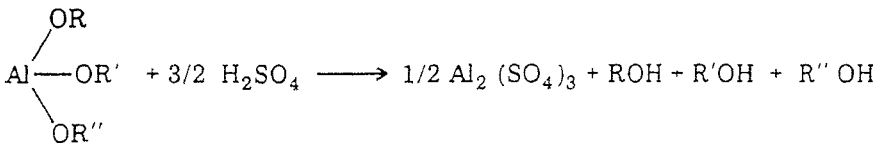


Figure 3.4 gives a flow diagram of the production of alcohols using these reactions.

Fatty Alcohols from Methyl Esters. Fats have long been basic raw materials for soaps and detergents. Such fats as are available are glyceryl esters of fatty acids (C_6 to C_{24}) and

have been hydrolyzed to the acids for soaps and reduced to the alcohols by catalytic hydro genation for detergents. The methyl esters of fatty acids[12] are also hydrogenated to fatt alcohols. These esters are prepared by reacting methanol with coconut or tallow triglyceride catalyzed by a small amount of sodium methylate. The refined oil is first dried by flashing a 150°C under a vacuum of 16.6 kPa, as otherwise it will consume relatively expensive sodiun methylate and also form soap. The methyl exchange esterification takes place in about a hour; then the reaction mix is settled and separated into an upper layer rich in ester an methanol and a lower layer rich in glycerin and methanol. The ester layer is washed coun tercurrently to remove excess methanol, to recover glycerin, and to remove the catalyst which would poison the hydrogenation. Yields of fatty alcohols are 90 to 95 percent.

Hydrogenation of methyl esters is catalyzed by a complex catalyst of copper II and coppe III chromite (made from copper nitrate, chromic oxide, and ammonia, with final roasting and is carried out at approximately 21 MPag and 260 to 315°C. The continuous equipmen used is outlined in Fig. 3.5 and consists of three vertical reactors 12 m high using 30 mol o heated hydrogen per mole of ester; the hydrogen serves not only for reducing but also fo heating and agitation. The crude alcohols are fractionated to the specified chain length.

SUDS REGULATORS. Suds regulation is often necessary for surfactants to do an efficient jol of cleaning in a washing machine. This is often achieved by combining different types such as anionics with nonionics, or anionics with soap. For soaps, foam inhibition increases with the amount of saturation and the number of carbons in the fatty acid residue. Soaps of satu rated C_{20-24} fatty acids are good foam inhibitors.[13] Other foam inhibitors are higher fatty acic

[12]ECT, 3d ed., vol. 1, 1978, p. 732.

[13]Sittig, op cit., p. 446.

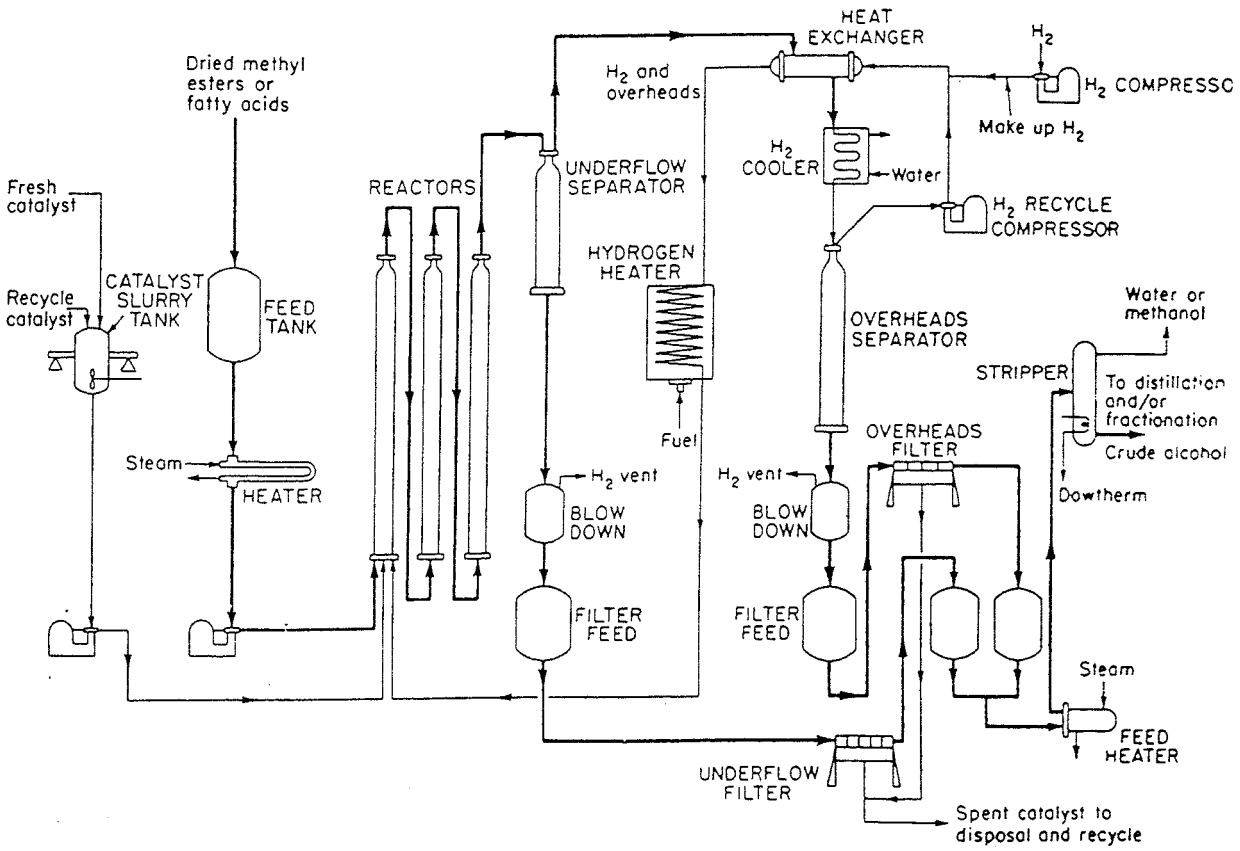


Fig. 3.5. Flowchart for the hydrogenolysis of methyl esters to obtain fatty alcohols and glycerin from natural fats. *(ECT, 3d ed., vol. 4, 1978, p. 837.)*

amides, aliphatic carboxylic acid esters containing at least 18 carbons in one or preferably both acid and alcohol chains, and *N*-alkylated aminotriazines.

BUILDERS. Builders boost detergent power. Complex phosphates, such as sodium tripolyphosphate, have been used most extensively. These are more than water softeners which sequester water-hardening calcium and magnesium ions. They prevent redeposition of soil from the wash water on fabrics. Proper formulation with complex phosphates has been the key to good cleaning with surfactants and made possible the tremendous development of detergents. Polyphosphates (e.g., sodium tripolyphosphate and tetrasodium pyrophosphate) have a synergistic action with the surfactant together with an enhanced effectiveness and hence reduce the overall cost. The rapid rise in the acceptance of detergents stemmed from the building action of the polyphosphates. During the 1960s the growth of algae and eutrophication in lakes became linked to the presence of phosphates in detergents. Several states restricted phosphate use so that substitutes had to be found. The first compound suggested was nitrilotriacetic acid (NTA), but it was declared a carcinogen in 1970. But new research results have vindicated its safety; in 1980 the EPA said it saw no reason to regulate NTA. This has not freed NTA for use because various congressional and environmental groups have challenged the EPA decision. There are no restrictions on its use in Canada.

Other builders are citrates, carbonates, and silicates. The newest, and seemingly most promising, substitute for phosphates is the use of zeolites.[14] By 1982 about 136 kt/year of zeolites were being used as detergent builders. The builder market is large and amounts to over 1000 kt annually. In 1980 phosphates accounted for 50 percent, zeolites 12 percent, silicates 13 percent, carbonates 12 percent, and NTA and citrates 2 percent each.

ADDITIVES. *Corrosion* inhibitors, such as sodium silicate, protect metal and washer parts, utensils, and dishes from the action of detergents and water. Carboxymethyl cellulose has been used as an *antiredeposition* agent. *Tarnish inhibitors* carry on the work of the corrosion inhibitor and extend protection to metals such as German silver. Benzotriazole has been used for this purpose. *Fabric brighteners* are fluorescent dyes which make fabrics look brighter because of their ability to convert ultraviolet light to visible light. Two dyes thus used are 4(2H-naphtho[1,2-d]triazol-2-yl)stilbene-2-sulfonate and disodium 4,4′-bis(4-anilino-6-morpholino-S-triazin-2-ylamino)-2,2′-stilbene disulfonate.

Bluings improve the whiteness of fabrics by counteracting the natural yellowing tendency. The ingredients used for this purpose can vary from the long-used ultramarine blue (bluing) to new dye materials. *Antimicrobial* agents include carbanilides, salicylanilides, and cationics. Peroxygen-type *bleaches* are also employed in laundry products. The use of *enzyme*-containing detergents has been common in Europe for several years and recently has been introduced into the United States. The enzymes decompose or alter the composition of soil and render the particles more easily removable. They are particularly useful in removing stains, particularly those of a protein nature.

Manufacture of Detergents

Table 31.5 compares three types of detergents. The most widely used detergent, a heavy-duty granule, is presented in Fig. 29.6, with the quantities of materials required. The reactions are:

[14]Layman, Detergents Shift Focus of Zeolites Market, *Chem. Eng. News* 60 (39) 10 (1982).

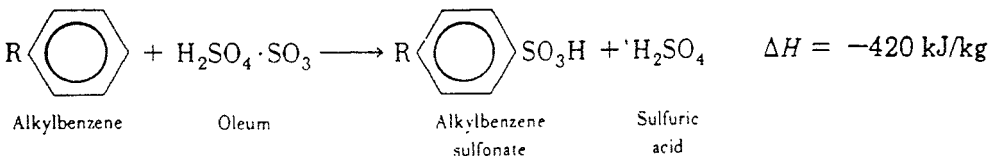
Table 3.5 Basic Composition of Three Types of Dry Phosphate-Based Detergents (Granules)

Ingredient	Function	Ingredient on Dry-Solids Basis, wt %: Light-Duty High Sudsers	Heavy-Duty Controlled Sudsers	Heavy-Duty High Sudsers
Surfactants				
Organic active, with suds regulators	Removal of oily soil, cleaning	25–40	8–20	20–35
Builders				
Sodium tripolyphosphate and/or tetrasodium pyrophosphate	Removal of inorganic soil, detergent-building	2–30	30–50	30–50
Sodium sulfate	Filler with building action in soft water	30–70	0–30	10–20
Soda ash	Filler with some building action	0	0–20	0–5
Additives				
Sodium silicate having $2.0 \leq SiO_2/Na_2O \leq 3.2$	Corrosion inhibitor with slight building action	0–4	6–9	4–8
Carboxymethyl cellulose	Antiredeposition of soil	0–0.5	0.5–1.3	0.5–1.3
Fluorescent dye	Optical brightening	0–0.05	0.05–0.1	~0.1
Tarnish inhibitors	Prevention of silverware tarnish	0	0–0.02	0–0.02
Perfume and sometimes dye or pigment	Aesthetic, improved product characteristics	0.1	0.1	0.1
Water	Filler and binder	1–5	2–10	3–10

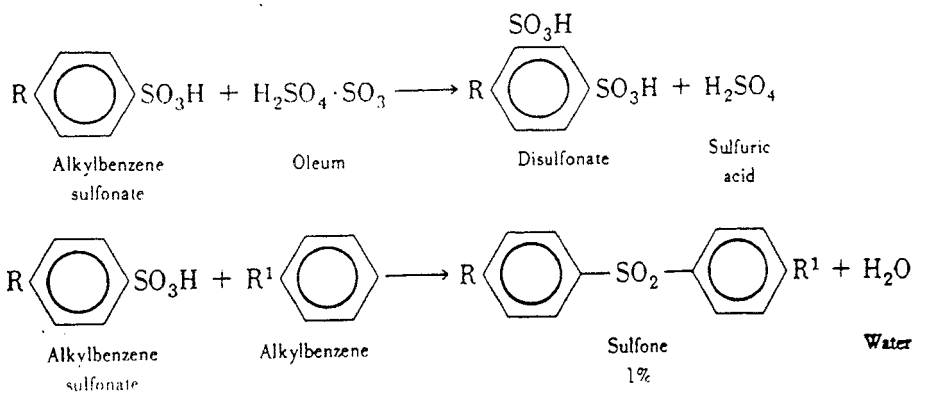
SOURCE: Van Wazer, *Phosphorus and Its Compounds*, vol. 2, Interscience, New York, 1961, p. 1760.

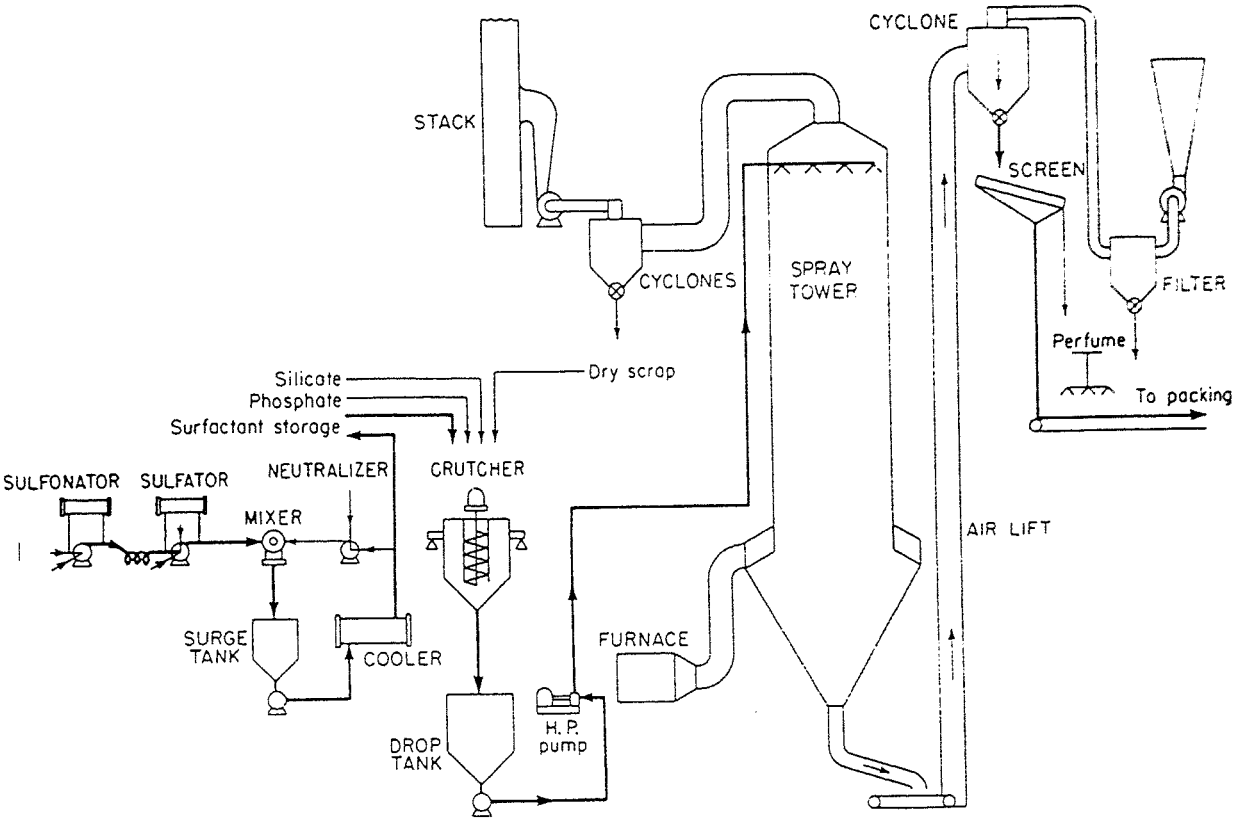
LINEAR ALKYLBENZENE SULFONATION

1. Main reaction:



2. Secondary reactions:





In order to produce 1 t of finished product, the following materials (in kilograms) are required:

Surfactant Materials		Corrosion Inhibitor	
Alkylbenzene (petrochemical)	75	Sodium silicate	125
Fatty alcohol (from tallow)	75	Builder	
Oleum	150	Sodium tripolyphosphate	500
NaOH solution	200	Miscellaneous additives	30
		Water	500

Fig. 3 .6. Simplified continuous flowchart for the production of heavy-duty detergent granules. *(Procter & Gamble Co.)*

FATTY ALCOHOL SULFATION

1. Main reaction:

$$R{-}CH_2OH + SO_3 \cdot H_2O \rightleftharpoons R'OSO_3H + H_2O \qquad \Delta H = -325 \text{ to } -350 \text{ kJ/kg}$$

2. Secondary reactions:

$$R{-}CH_2OH + R'{-}CH_2{-}OSO_3H \rightarrow R{-}CH_2{-}O{-}CH_2{-}R' + H_2SO_4$$
$$R'{-}CH_2{-}CH_2OH + SO_3 \rightarrow R'{-}CH{=}CH_2 + H_2SO_4$$
$$R{-}CH_2OH + SO_3 \rightarrow RCHO + H_2O + SO_2$$
$$R{-}CH_2OH + 2SO_3 \rightarrow RCOOH + H_2O + 2SO_2$$

This presentation is supplemented by Table 3 .5, which gives the basic constituents in more detail for the three types of detergent granules. The continuous flowchart in Fig. 3 .6 can be broken down into the following coordinated sequences:

Sulfonation-sulfation. The alkylbenzene (AB) is introduced continuously into the sulfonator with the requisite amount of oleum, using the dominant bath principle shown in Fig. 29.8 to control the heat of sulfonation conversion and maintain the temperature at about 55°C. Into the sulfonated mixture is fed the fatty tallow alcohol and more of the oleum. All are pumped through the sulfater, also operating on the dominant bath principle, to maintain the temperature at 50 to 55°C, thus manufacturing a mixture of surfactants.

Neutralization. The sulfonated-sulfated product is neutralized with NaOH solution under controlled temperature to maintain fluidity of the surfactant slurry. The surfactant slurry is conducted to storage.

The surfactant slurry, the sodium tripolyphosphate, and most of the miscellaneous additives are introduced into the crutcher. A considerable amount of the water is removed, and the paste is thickened by the tripolyphosphate hydration reaction:

$$\underset{\text{Sodium tripolyphosphate}}{Na_5P_3O_{10}} + 6H_2O \longrightarrow \underset{\text{Sodium tripolyphosphate hexahydrate}}{Na_5P_3O_{10}\cdot 6H_2O}$$

This mixture is pumped to an upper story, where it is *sprayed* under high pressure into the 24-m-high spray tower, counter to hot air from the furnace. Dried granules of acceptable shape and size and suitable density are formed. The dried granules are transferred to an upper story again by an air lift which cools them from 115°C and stabilizes the granules. The granules are separated in a cyclone, screened, perfumed, and packed.

The sulfonation conversion is shown in Fig. 3.7 to be extremely fast. The reactions also need to have the high heats of reaction kept under control, as shown in more detail in Fig. 29.8, depicting the circulating heat exchanger, or dominant baths, for both these chemical conversions and for neutralization. The use of oleum in both cases reduces the sodium sulfate in the finished product. However, the oleum increases the importance of control to prevent oversulfonation. In particular, alkylbenzene sulfonation is irreversible and results in about 96 percent conversion in less than a minute when run at 55°C with 1 to 4% excess SO_3 in the oleum. A certain minimum concentration of SO_3 in the oleum is necessary before the sulfonation reaction will start, which in this case is about 78.5% SO_3 (equivalent to 96% sulfuric acid). As both these reactions are highly exothermic and rapid, efficient heat removal is required to prevent oversulfonation and darkening. Agitation is provided by a centrifugal pump, to which the oleum is admitted. The recirculation ratio (volume of recirculating material divided by the volume of throughput) is at least 20:1 to give a favorable system. To provide the sulfonation time to reach the desired high conversion, more time is allowed by conducting the mixture through a coil, where time is given for the sulfonation reaction to go to completion.

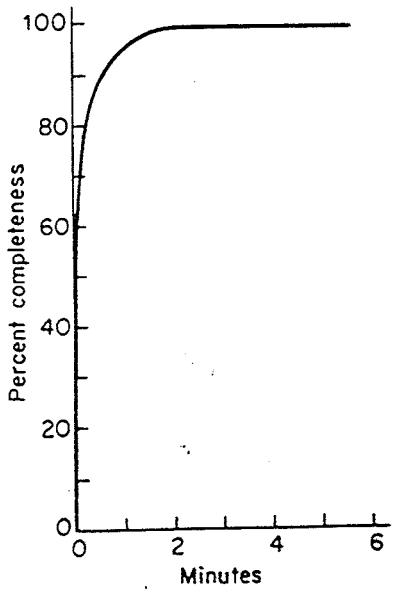


Fig. 3.7. Alkylbenzene sulfonation completeness versus time at 55°C. *(Procter & Gamble Co.)*

Neutralization of the acid slurry releases six to eight times as much heat as the sulfonation reaction. Here a

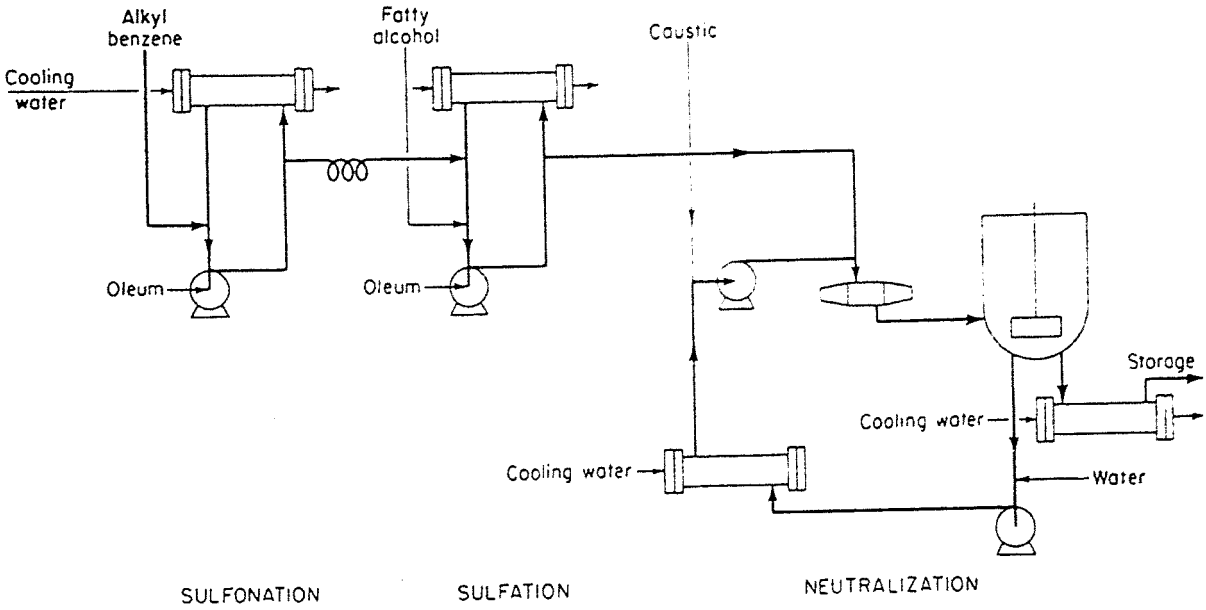


Fig. 3.8. Continuous series sulfonation-sulfation, ending with neutralization, in the circulating heat-exchanging dominant bath to control heat. *(Procter & Gamble Co.)*

dominant bath (Fig. 3.8) is employed which quickly effects the neutralization, since a partly neutralized acid mix is very viscous.

SOAP

Soap comprises the sodium or potassium salts of various fatty acids, but chiefly of oleic, stearic, palmitic, lauric, and myristic acids. For generations its use has increased until its manufacture has become an industry essential to the comfort and health of civilized human beings. The relative and overall production of soap and detergents is shown by the curve in Fig. 3.1. History and industrial statistics are discussed in the first part of this chapter (Table 3.1).

Raw Materials

Tallow is the principal fatty material in soapmaking; the quantities used represent about three-fourths of the total oils and fats consumed by the soap industry, as shown in Fig. 3.1. It contains the mixed glycerides obtained from the solid fat of cattle by steam rendering. This solid fat is digested with steam; the tallow forms a layer above the water, so that it can easily be removed. Tallow is usually mixed with coconut oil in the soap kettle or hydrolyzer in order to increase the solubility of the soap. Greases (about 20 percent) are the second most important raw material in soapmaking. They are obtained from hogs and smaller domestic animals and are an important source of glycerides of fatty acids. They are refined by steam rendering or by solvent extraction and are seldom used without being blended with other fats. In some

cases, they are treated so as to free their fatty acids, which are used in soap instead of the grease itself. Coconut oil has long been important. The soap from coconut oil is firm and lathers well. It contains large proportions of the very desirable glycerides of lauric and myristic acids. Free fatty acids are utilized in soap, detergent, cosmetic, paint, textile, and many other industries. The acidification of "foots," or stock resulting from alkaline refining of oils, also produces fatty acids. The important general methods of splitting are outlined in Table 3.4. The Twitchell process is the oldest.[15] Continuous countercurrent processes are now most commonly used.

The soapmaker is also a large consumer of chemicals, especially caustic soda, salt, soda ash, and caustic potash, as well as sodium silicate, sodium bicarbonate, and trisodium phosphate. Inorganic chemicals added to the soap are the so-called builders. Important work by Harris of Monsanto and his coworkers[16] demonstrated conclusively that, in particular, tetrasodium pyrophosphate and sodium tripolyphosphate were unusually effective synergistic soap builders. Of considerable economic importance was the demonstration that combinations of inexpensive builders, such as soda ash, with the more effective (and expensive) tetrasodium pyrophosphate or sodium tripolyphosphate, were sometimes superior to the phosphate used alone. It was further shown that less soap could be used in these mixtures to attain the same or more effective soil removal.

Manufacture

The manufacture of soap is presented in Fig. 3.3. The long-established kettle[17] process, however, is mainly used by smaller factories or for special and limited production. As soap technology changed, continuous alkaline saponification was introduced. Computer control allows an automated plant for continuous saponification by NaOH of oils and fats to produce in 2 h the same amount of soap (more than 300 t/day) made in 2 to 5 days by traditional batch methods.

The present procedure involves continuous splitting, or hydrolysis, as outlined in Table 3.2 and detailed in Fig. 3.3. After separation of the glycerin, the fatty acids are neutralized to soap.

The basic chemical reaction in the making of soap is saponification.[18]

$$\underset{\text{Caustic soda}}{3NaOH} + \underset{\text{Glyceryl stearate}}{(C_{17}H_{35}COO)_3C_3H_5} \rightarrow \underset{\text{Sodium stearate}}{3C_{17}H_{35}COONa} + \underset{\text{Glycerin}}{C_3H_5(OH)_3}$$

[15]This process is described in more detail in CPI 2, p. 619.

[16]*Oil Soap* 19 3 (1942); Cobbs et al., *Oil Soap* 17 4 (1940); Wan Wazer, "Phosphorus and Its Compounds," chap. 27, in *Detergent Building*, Interscience, New York, 1958.

[17]Full descriptions with flowcharts for the kettle process full-boiled (several days), semi-boiled, and cold are available on pp. 623–625 of CPI 2.

[18]Although stearic acid is written in these reactions, oleic, lauric, or other constituent acids of the fats could be substituted. See Table 28.1 for fatty acid composition of various fats and oils.

The procedure is to split, or hydrolyze, the fat, and then, after separation from the valuable glycerin, to neutralize the fatty acids with a caustic soda solution:

$$\underset{\text{Glyceryl stearate}}{(C_{17}H_{35}COO)_3C_3H_5} + 3H_2O \rightarrow \underset{\text{Stearic acid}}{3C_{17}H_{35}COOH} + \underset{\text{Glycerin}}{C_3H_5(OH)_3}$$

$$\underset{\text{Stearic acid}}{C_{17}H_{35}COOH} + \underset{\text{Caustic soda}}{NaOH} \rightarrow \underset{\text{Sodium stearate}}{C_{17}H_{35}COONa} + H_2O$$

The usual fats and oils of commerce are not composed of the glyceride of any one fatty acid, but of a mixture. However, some individual fatty acids of 90% purity or better are available from special processing. Since the solubility and hardness of the sodium salts (Table 3.6) of the various fatty acids differ considerably, the soapmaker chooses the raw material according to the properties desired, with due consideration of the market price.

In continuous, countercurrent splitting the fatty oil is deaerated under a vacuum to prevent darkening by oxidation during processing. It is charged at a controlled rate to the bottom of the hydrolyzing tower through a sparge ring, which breaks the fat into droplets. These towers, about 20 m high and 60 cm in diameter, are built of Type 316 stainless steel (see Fig. 3.5). The oil in the bottom contacting section rises because of its lower density and extracts the small amount of fatty material dissolved in the aqueous glycerin phase. At the same time daerated, demineralized water is fed to the top contacting section, where it extracts the glycerin dissolved in the fatty phase. After leaving the contacting sections, the two streams enter the reaction zone.[19] Here they are brought to reaction temperature by the direct injection of high-pressure steam, and then the final phases of splitting occur. The fatty acids are discharged from the top of the splitter or hydrolyzer to a decanter, where the entrained water is separated or flashed off. The glycerin-water solution is then discharged from the bottom of an automatic interface controller to a settling tank. See Fig. 3.10 for glycerin processing.

Although the crude mixtures of fatty acids resulting from any of the above methods may be used as such, usually a separation into more useful components is made. The composition of the fatty acids from the splitter depends upon the fat or oil from which they were derived.

[19]Allen et al., Continuous Hydrolysis of Fats, *Chem. Eng. Prog.*, 43 459 (1947); Fatty Acids, *Chem. Eng.* 57 (11), 118 (1950); Ladyn, Fat Splitting, *Chem. Eng.* 71 (17) 106 (1964) (continuous flowcharts).

Table 3.6 Solubilities of Various Pure Soaps (in grams per 100 g of water at 25°C)

	Stearate	Oleate	Palmitate	Laurate
Sodium	0.1*	18.1	0.8*	2.75
Potassium	—	25.0	—	70.0*
Calcium	0.004†	0.04	0.003	0.004†
Magnesium	0.004	0.024	0.008	0.007
Aluminum	*i*	*i*	*d*	

*Approximate.
†Solubility given at 15°C only.
NOTE: *i* indicates that the compound is insoluble; *d* indicates decomposition.

Those most commonly used for fatty acid production include beef tallow and coconut, palm, cottonseed, and soybean oil. Probably the most used of the older processes is panning and pressing. This fractional crystallization process is limited to those fatty acid mixtures which solidify readily, such as tallow fatty acid. The molten fatty acid is run into pans, chilled, wrapped in burlap bags, and pressed. This expression extracts the liquid red oil (mainly oleic acid), leaving the solid stearic acid. The total number of pressings indicates the purity of the product. To separate fatty acids of different chain lengths, distillation[20] is employed, vacuum distillation being the most widely used. Three fractionating towers of the conventional tray type are operated under a vacuum. Preheated, crude fatty acid stock is charged to the top of a stripping tower. While it is flowing downward, the air, moisture, and low-boiling fatty acids are swept out of the top of the tank. The condensate, with part of it redrawn as a reflux, passes into the main fractionating tower, where a high vacuum is maintained at the top. A liquid side stream, also near the top, removes the main cut (low-boiling acids), while overheads and noncondensables are withdrawn. The liquid condensate (high-boiling acids) is pumped to a final flash tower, where the overhead distillate is condensed and represents the second fatty acid fraction. The bottoms are returned to the stripping tower, reworked, and removed as pitch. The fatty acids may be sold as such or converted into many new chemicals.

The energy requirements that enter into the cost of producing soap are relatively unimportant in comparison with the cost of raw materials, packaging, and distribution. The energy required to transport some fats and oils to the soap factory is occasionally considerable. The reaction that goes on in the soap reactor is exothermic.

The following are the principal sequences into which the making of bar soap by water splitting and neutralization can be divided, as shown by the flowchart in Fig. 3.3.

Transportation of fats and oils.

Transportation and manufacture of caustic soda.

Blending of the catalyst, zinc oxide, with melted fats and heating with steam takes place in the blend tank.

Hot melted fats and catalysts are introduced into the bottom of the hydrolyzer.

Splitting of fats takes place countercurrently in the hydrolyzer at 250°C and 4.1 MPa, continuously, the fat globules rising against a descending aqueous phase.

The aqueous phase, having dissolved the split glycerin (about 12%), falls and is separated.

The glycerin water phase is evaporated and purified. See Glycerin.

The fatty acids phase at the top of the hydrolyzer is dried by flashing off the water and further heated.

In a high-vacuum still the fatty acids are distilled from the bottoms and rectified.

The soap is formed by continuous neutralization with 50% caustic soda in high-speed mixer-neutralizer.

The neat soap is discharged at 93°C into a slowly agitated blending tank to even out any inequalities of neutralization. At this point the neat soap analyzes: 0.002 to 0.10% NaOH, 0.3 to 0.6% NaCl, and approximately 30% H_2O. This neat soap may be extruded, milled, flaked, or spray-dried, depending upon the product desired. The flowchart in Fig. 29.3 depicts the finishing operations for floating bar soap.

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[20]Fatty Acid Distillation, *Chem. Eng.* 55 146 (1948). Pictured flowcharts of both straight and fractional distillation; Marsel and Allen, Fatty Acid Processing, *Chem. Eng.* 54 (6) 104 (1947); ECT, 3d ed., vol. 4, 1978, p. 839.

These finishing operations are detailed: The pressure on the neat soap is raised to 3.5 MPa, and the soap is heated to about 200°C in a high-pressure steam exchanger. This heated soap is released to a flash tank at atmospheric pressure, where a partial drying (to about 20%) takes place because the soap solution is well above its boiling point at atmospheric pressure. This viscous, pasty soap is mixed with the desired amount of air in a mechanical scraped-wall heat exchanger, where the soap is also cooled by brine circulation in the outer shell from 105°C to about 65°C. At this temperature the soap is continuously extruded in strip form and is cut into bar lengths. Further cooling, stamping, and wrapping complete the operation. This entire procedure requires only 6 h, as compared with over a week for the kettle process. The main advantages of soap manufactured by this process as compared with the kettle process are (1) improved soap color from a crude fat without extensive pretreatment, (2) improved glycerin recovery, (3) flexibility in control, and (4) less space and labor. Intimate molecular control is the key to the success of this continuous process, as, for example, in the hydrolyzer, where the desired mutual solubility of the different phases is attained by appropriate process conditions.

Typical Soaps

The main classes of soap are toilet soaps and industrial soaps. These different soaps can frequently be made by one or more of the procedures described. The bar soap[21] market consists of regular and superfatted toilet soaps, deodorant and/or antimicrobial soaps, floating soaps, transparent/translucent, marbelized, and hard water soaps. Some overlapping occurs as some deodorant bars have a superfatted base. Toilet soap is usually made from mixtures of tallow and coconut oil in ratios of 80/20 or 90/10, and superfatted soaps have ratios of 50/50 or 60/40 and some have 7 to 10% free fatty acid added as well. Deodorant soaps contain an agent such as 3,4′,5-tribromosalicylanilide (TBS) which prevents the decomposition of perspiration into odorous compounds.

Practically all soap merchandised contains from 10 to about 30% water. If soap were anhydrous, it would be too hard to dissolve easily. See Table 3.6. Almost all soaps contain perfume, even though it is not apparent, serving merely to disguise the original soapy odor. Toilet soaps are made from selected materials and usually contain only 10 to 15% moisture; they have very little added material, except for perfume and perhaps a fraction of a percent of titanium dioxide as a whitening agent. Shaving soaps contain a considerable proportion of potassium soap and an excess of stearic acid, the combination giving a slower-drying lather. "Brushless" shaving creams contain stearic acid and fats with much less soap.

Another type of bar soap (in comparison with the floating type in Fig. 3.3) is milled toilet soap. The word milled refers to the fact that, during processing, the soap goes through several sets of heavy rolls, or mills, which mix and knead it. Because of the milling operation, the finished soap lathers better and has a generally improved performance, especially in cool water. The milling operation is also the way in which fragrant perfumes are incorporated into cold soap. If perfume were mixed with warm soap, many of the volatile scents would evaporate. After the milling operation, the soap is pressed into a smooth cylinder and is extruded continuously. It is then cut into bars, stamped, and wrapped as depicted in Fig. 3.9.

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[21]Jungerman, New Trends in Bar Soap Technology, *Soap Cosmet. Chem. Spec.* 58 (1) 31 (1982).

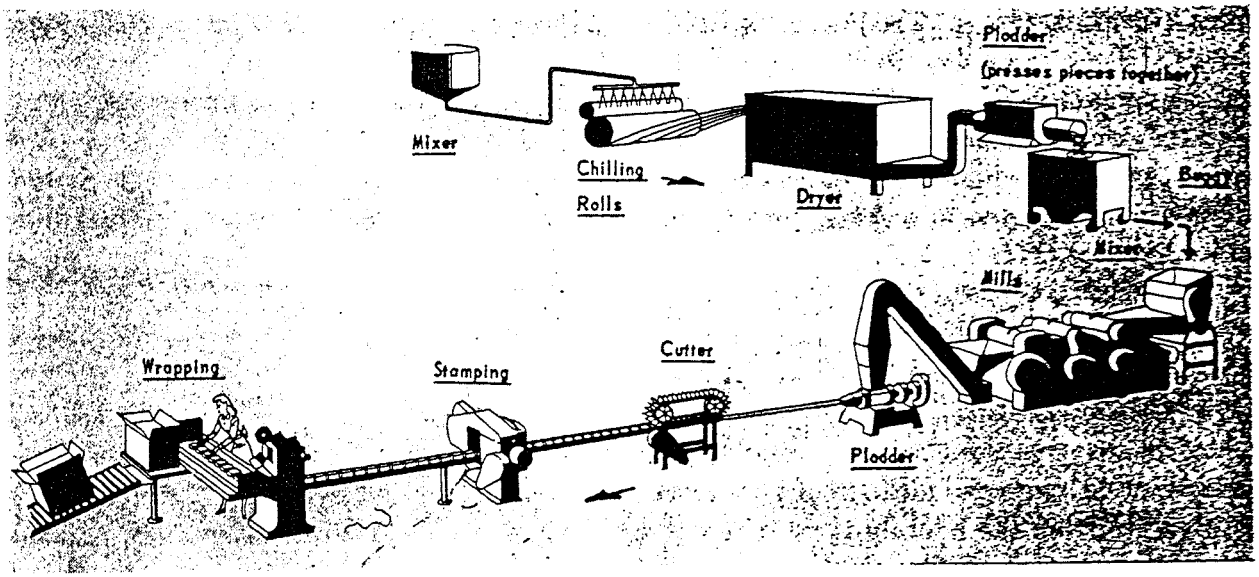

Fig. 3.9. Making soap in milled bars. Another type of bar soap (in comparison with the floating type shown in Fig. 3.3) is milled toilet soap. The word "milled" refers to the fact that, during processing, the soap goes through several sets of heavy rolls or mills which mix and knead it. A much more uniform product is obtained, and much direct labor is saved.

Crystal Phases in Bar Soap. The physical properties of bar soap are dependent upon the crystalline soap phases present and the condition of these phases. Any of three or more phases may exist in sodium soaps, depending upon the fat used, the moisture and electrolyte composition of the system, and the processing conditions. Milled toilet soaps are mechanically worked to transform the omega phase, at least partially, to the translucent beta phase producing a harder, more readily soluble bar. Extruded floating soaps contain both crystals formed in the freezer and crystals that grow from the melt after it leaves the freezer. Processing conditions are adjusted for an optimum proportion of crystallized matrix, which adds strength and rigidity to the bar. If necessary, the bar may be tempered by reheating to strengthen it.

GLYCERIN

HISTORICAL. Glycerin[22] is a clear, nearly colorless liquid having a sweet taste but no odor. Scheele first prepared glycerin in 1779 by heating a mixture of olive oil and litharge. On washing with water, a sweet solution was obtained, giving, on evaporation of the water, a viscous heavy liquid, which the discoverer called "the sweet principle of fats." In 1846 Sobrero produced the explosive nitroglycerin for the first time, and in 1868 Nobel, by absorbing it in kieselguhr, made it safe to handle as dynamite. These discoveries increased the demand for glycerin. This was in part satisfied by the development in 1870 of a method for recovering glycerin and salt from spent soap lyes. Since about 1948, glycerol has been produced from petrochemical raw materials by synthetic processes.

[22]The term *glycerin* is chosen for the technical product containing the pure trihydroxy alcohol *glycerol*. The spelling of glycerin is that employed by the USP.

USES AND ECONOMICS. The production of crude glycerin is approximately 150 kt/year. Synthetic glycerin furnishes about 40 percent of the market. Glycerin is supplied in several grades, including USP and CP, grades which are chemically pure, contain not less than 95% glycerol, and are suitable for resins and other industrial products. Yellow distilled is used for certain processes where higher-purity types are not essential, e.g., as a lubricant in tire molds. Glycerin is employed in making, preserving, softening, and moistening a great many products, as shown in Table 3.7.

Manufacture

Glycerin may be produced by a number of different methods, of which the following are important: (1) the saponification of glycerides (oils and fats) to produce soap, (2) the recovery of glycerin from the hydrolysis, or splitting, of fats and oils to produce fatty acids, and (3) the chlorination and hydrolysis of propylene and other reactions from petrochemical hydrocarbons.

In recovering glycerin from soap plants, the energy requirements are mostly concerned with heat consumption involved in the unit operations of evaporation and distillation, as can be seen by the steam requirements on the flowchart in Fig. 29.10. The breakdown of natural and synthetic procedures for glycerin is:

Glycerin from Sweet Water from Hydrolyzer	Glycerin from Petroleum
Evaporation (multiple effect) for concentration	Purification of propylene
Purification with settling	Chlorination to allyl chloride
Steam vacuum distillation	Purification and distillation
Partial condensation	Chlorination with HOCl
Decoloration (bleaching)	Hydrolysis to glycerin
Filtration or ion-exchange purification	Distillation

RECOVERY FROM FATTY ACIDS. Practically all natural glycerin is now produced as a coproduct of the direct hydrolysis of triglycerides from natural fats and oils. Hydrolysis is

Table 3.7 Glycerin Consumption (metric kilotons)

	1978	1980
Alkyd resins	21.5	27
Cellophane	6.4	8
Tobacco	14.2	25
Explosives	2.9	3
Drugs and cosmetics	24.1	38
Urethane foams	13.8	18
Foods and beverages	14.8	24
Miscellaneous	15.8	16

SOURCE: ECT, 3d ed., vol. 11, 1980, p. 927; *Chem. Mar. Rep*, May 25, 1981.

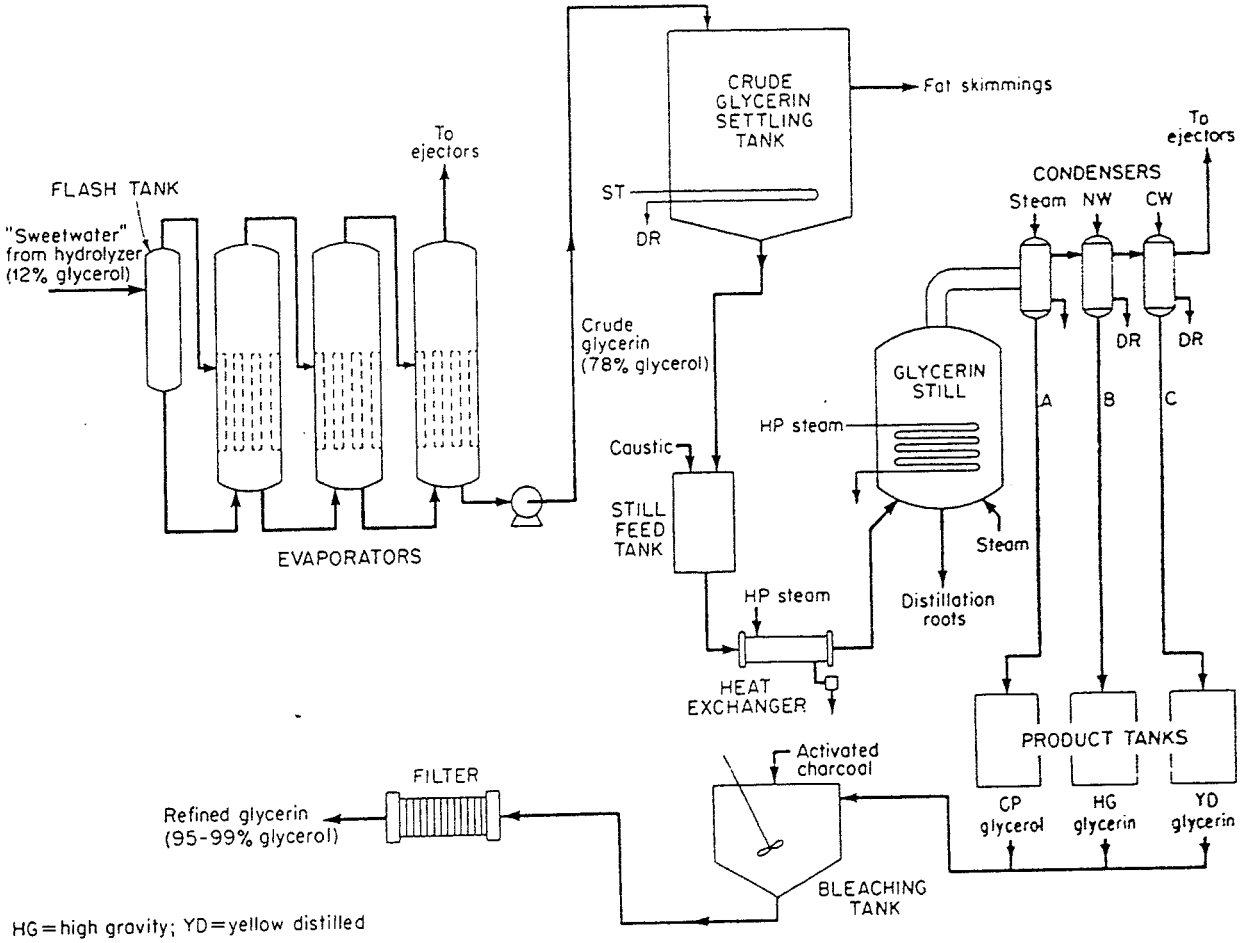

Fig. 3.10. Flowchart for glycerin manufacture from hydrolysis of sweet water *(Procter & Gamble Co.)*

carried out in large continuous reactors at elevated temperatures and pressures with a catalyst. Water flows countercurrent to the fatty acid and extracts glycerol from the fatty phase. The sweet water from the hydrolyzer column contains about 12% glycerol. Evaporation of the sweet water from the hydrolyzer is a much easier operation compared with evaporation of spent soap lye glycerin in the kettle process. The high salt content of soap lye glycerin requires frequent soap removal from the evaporators. Hydrolyzer glycerin contains practically no salt and is readily concentrated. The sweet water is fed to a triple-effect evaporator, as depicted by the flowchart in Fig. 3.10, where the concentration is increased from 12% to 75 to 80% glycerol. Usually, no additional heat (other than that present in the sweet-water effluent from the hydrolyzer) is required to accomplish the evaporation. After concentration of the sweet water to hydrolyzer crude, the crude is settled for 48 h at elevated temperatures to reduce fatty impurities that could interfere with subsequent processing. Settled hydrolyzer crude contains approximately 78% glycerol, 0.2% total fatty acids, and 22% water. The settled crude is distilled under a vacuum (8 kPa) at approximately 200°C. A small amount of caustic is usually added to the still feed to saponify fatty impurities and reduce the possibility of codistillation with the glycerol. The distilled glycerin is condensed in three stages at decreasing temperatures. The first stage yields the purest glycerin, usually 99% glycerol, meeting CP specifications. Lower-quality grades of glycerin are collected in the second and third condensers. Final purification of glycerin is accomplished by carbon bleaching, followed by filtration or ion exchange.

SYNTHETIC GLYCERIN.[23] The growing market for glycerin, and the fact that it was a coproduct of soap and dependent upon the latter's production, were the incentives for research into methods for producing this trihydroxy alcohol. The process of making glycerin from propylene procured for the Shell Development Co. the 1948 Chemical Engineering achievement award.[24] The propylene is chlorinated at 510°C at 101 kPa to produce allyl chloride in seconds in amounts greater than 85 percent of theory (based on the propylene). Vinyl chloride, some disubstituted olefins, and some 1, 2 and 1, 3-dichloropropanes are also formed. (The reaction producing allyl chloride was new to organic synthesis, involving the chlorination of an olefin by substitution instead of addition.) Treatment of the allyl chloride with hypochlorous acid at 38°C produces glycerin dichlorohydrin ($CH_2Cl \cdot CHCl \cdot CH_2OH$), which can be hydrolyzed by caustic soda in a 6% Na_2CO_3 solution at 96°C. The glycerin dichlorohydrin can be hydrolyzed directly to glycerin, but this takes two molecules of caustic soda; hence a more economical procedure is to react with the cheaper calcium hydroxide, taking off the epichlorohydrin as an overhead in a stripping column. The epichlorohydrin is

[23]ECT, 3d ed., vol. 11, 1980, p. 923; *McGraw-Hill Encyclopedia of Science and Technology*, 5th ed., vol. 16, McGraw-Hill, New York, 1982, p. 310.

[24]Hightower, Glycerin from Petroleum, *Chem. Eng.* 55 (9) 96 (1948); Synthetic Glycerin, *Chem. Eng.* 55 (10) 100 (1948).

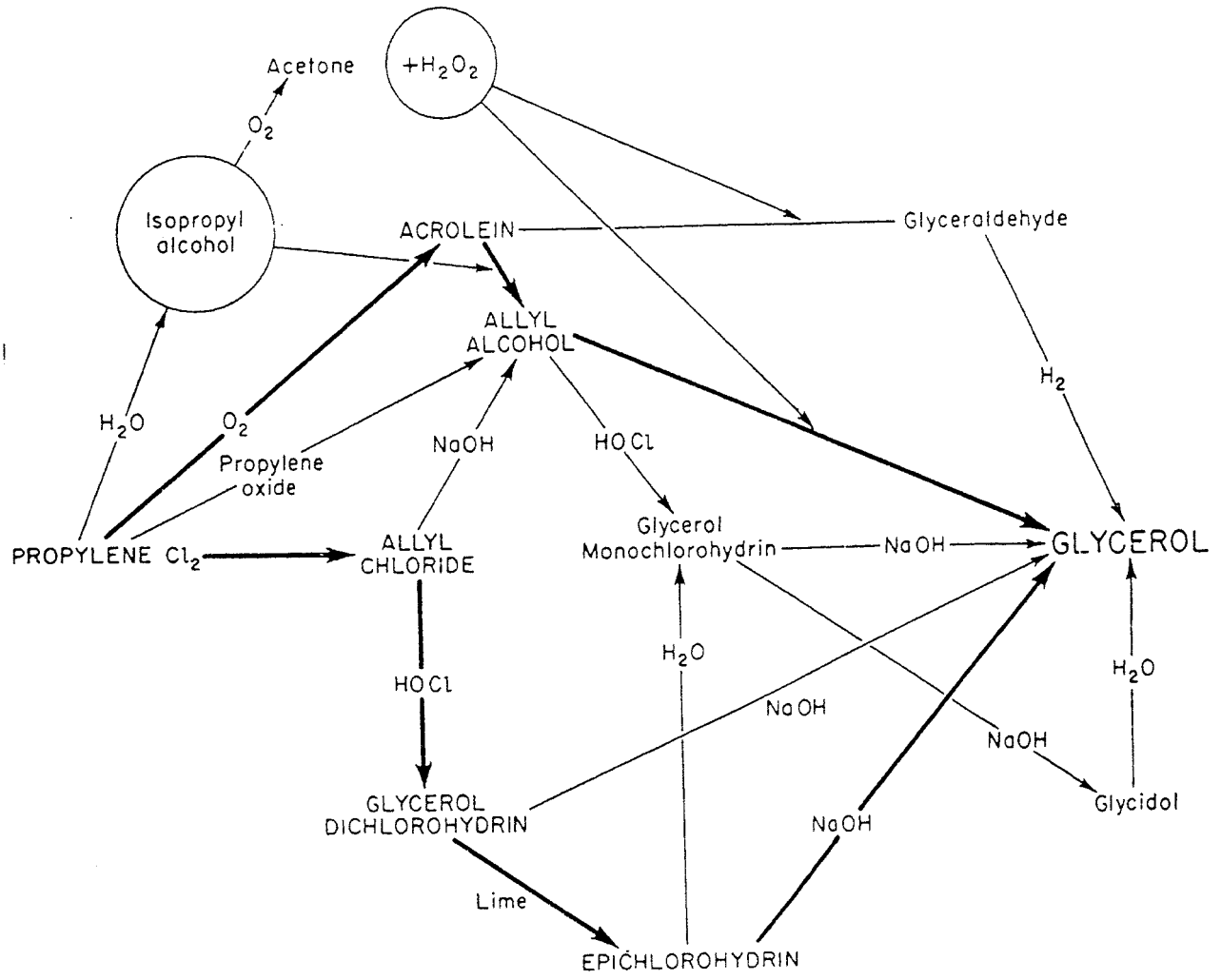

Fig. 3.11. Routes for the synthesis of glycerin.

easily hydrated to monochlorohydrin and then hydrated to glycerin with caustic soda. The reactions are:

$$CH_3 \cdot CH{:}CH_2 + Cl_2 \rightarrow CH_2Cl \cdot CH{:}CH_2 + HCl \text{ (85 percent yield)}$$
$$CH_2Cl \cdot CH{:}CH_2 + HOCl \rightarrow CH_2Cl \cdot CHCl \cdot CH_2OH \text{ (95 percent yield)}$$
$$CH_2Cl \cdot CHCl \cdot CH_2OH + 2NaOH \rightarrow CH_2OH \cdot CHOH \cdot CH_2OH + 2NaCl$$

The overall yield of glycerin from allyl chloride is above 90 percent.

Another process for obtaining glycerin from propylene involves the following reactions, where isopropyl alcohol and propylene furnish acetone and glycerin (through acrolein) in good yields.

$$CH_3 \cdot CHOH \cdot CH_3 + \text{air} \rightarrow CH_3 \cdot CO \cdot CH_3 + H_2O_2$$
$$CH_3 \cdot CH{:}CH_2 + \text{air} \rightarrow CHO \cdot CH{:}CH_2 + H_2O$$
$$CHO \cdot CH{:}CH_2 + H_2O_2 \rightarrow CHO \cdot CHOH \cdot CH_2OH \rightarrow CH_2OH \cdot CHOH \cdot CH_2OH$$

Figure 29.11 illustrates the various methods of synthetic glycerin production.

In 1982 only Dow Chemical Co. was producing synthetic glycerin the the United States because of rising energy costs and the increase in supplies from soapmakers and imports of low-priced glycerin from Europe.

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Chapter 4

Fermentation Industries

HISTORICAL. Although the fermentation of fruits to alcohol was known to primitive humans, and although the making of various beverages out of fruits and grains has been well established for centuries, only during the past century has wider application of this procedure been recognized. Now scientists are directing the life processes of yeasts, bacteria, and molds to produce chemicals. The modern definition of industrial fermentation is any microbial process controlled by humans that produces useful products.

The foundation of the scientific understanding of fermentation, indeed of the action of all microorganisms, hence of their economic control, rests firmly upon the genius of one man, Louis Pasteur.[1] He showed that fermentation is directly caused by the life processes of minute organisms. By understanding how these microorganisms function and by recognizing that varieties of yeasts, for example, act differently and that the environment fundamentally affects even a given strain, these processes of fermentation can be controlled in an exact scientific manner.

(Microorganisms, which include bacteria, yeasts, and molds, feed upon organic materials. It is this feeding that interests the manufacturer, for if they are supplied with the necessary energy foods, together with other needed nutrients, these microvegetative organisms will not only grow and multiply but will change the food into other chemical substances.)

Yeasts and bacteria are unicellular and of very small dimensions. Yeasts are irregularly oval and around 0.004 to 0.010 mm in diameter. Bacteria are smaller, mostly less than 0.007 mm in the longer dimension, and more diverse in shape. Many of them, bacilli, are rod-shaped. Yeasts multiply by budding, and bacteria by binary fission. Molds are multicellular filaments and increase by vegetative growth of the filament. Sporulation provides for the next cycle, as it does also with many bacteria. The vegetative reproduction cycle of these bacteria and of yeast is short—measured in minutes. Because of this, they multiply exceedingly fast.

The production of lactic acid in 1880 was the beginning of industrial fermentation to produce a useful product other than alcohol. During World War I, Chaim Weizmann developed a fermentation process to convert corn to acetone and *n*-butanol. Acetone was necessary for the manufacture of cordite for use in ammunition and without this fermentation process Britain would have had a serious shortage of ammunition. Citric acid and gluconic acid were successfully produced between 1920 and 1940, but the young petrochemical industry then made most fermentation processes uneconomical. During World War II, the discovery of antibiotics, such as penicillin, set the stage for the great technological advances in controlling microbiological processes that are commonly used today.

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[1]Current Developments in Fermentation, *Chem. Eng.* 81 (26) 98 (1974); ECT, 3d ed., vol. 9, 1980, pp. 861–880.

USES AND ECONOMICS. Many fermentation processes are in direct competition with strictly chemical syntheses. Alcohol, acetone, butyl alcohol, and acetic acid produced by fermentation have largely been superseded by their synthetic counterparts. Almost all the major antibiotics are obtained from fermentation processes. Dextran is another fermentation product. The microbiological production of vitamins has also become economically important. In Chap. 6 antibiotics, hormones, and vitamins are presented together with several flowcharts. Table 4.1 lists some of the products produced by fermentations. The enzyme glucose isomerase is used to produce high fructose syrup from corn, and proteases produced from mold enzymes are used to coagulate protein in milk to produce cheese.

Fermentation under controlled conditions involves chemical conversions.[2] Some of the more important processes are: *oxidation*, e.g., alcohol to acetic acid, sucrose to citric acid,

[2]Wailen, Stodola, and Jackson, *Type Reactions in Fermentation Chemistry*, Dept. of Agriculture, Agricultural Research, 1959 (hundreds of reactions under 14 types).

***Table* 4.1** Survey of Some Important Fermentations

Food and Beverages	Industrial	Pharmaceuticals (antibiotics)
Beer (Y)	Acetic acid	Amphotericin
Bread (Y)	Acetone	Bacitracin
Cheese (M or B)	Amino acids	Bleomycin
Cocoa (B and Y)	Aspartic acid	Candicidin
Coffee (M)	2,3-Butanediol	Capreamycin
MSG (B)	*n*-Butyl alcohol	Cephalosporin C
Olives (B)	Carbon dioxide	Chloramphenicol
Pickles (B and Y)	Citric acid	Chlortetracycline
Sauerkraut (B)	Dextran	Colistin
Single-cell protein (Y, B, or M)	Dihydroxyacetone	Cycloheximide
Tea	Ethyl alcohol	Cycloserine
Vinegar (B and Y)	Fumaric acid	Dactinomycin
Wine (Y)	Fusel oil	Doxorubicin
Whiskey	Gallic acid	Erythromycin
Vitamins	Gluconic acid	Gentamycin
Ergosterol (Y, M)	Glycerol	Griseofulvin
Gibberellins (B)	Isoleucine	Kanamycin
Riboflavin (B, Y)	Itaconic acid	Lincomycin
Vitamin A (B)	2-Ketogluconic acid	Mithramycin
Vitamin B_2 (Y)	5-Ketogluconic acid	Mitomycin C
Vitamin B_{12} (B, M)	Lactic acid	Neomycin
Enzymes	Lysine	Novobiocin
Amylases	Succinic acid	Nystatin
Cellulase	Sulfuric acid (from sulfur)	Oleandromycin
Dextranase	Tartaric acid	Oxytetracycline
Glucose isomerases	Valine	Paromomycin
Lactase	Yeast	Penicillins
Invertase	Xanthan	Polymyxin
Maltase		Rigamycin
Pectinase		Spectinomycin
Proteases		Streptomycins
		Tetracycline
		Vancomycin

Y, Yeast; B, bacteria; M, molds.

and dextrose to gluconic acid; *reduction*, e.g., aldehydes to alcohols (acetaldehyde to ethyl alcohol), and sulfur to hydrogen sulfide; *hydrolysis*, e.g., starch to glucose, and sucrose to glucose and fructose and on to alcohol; and *esterification*, e.g., hexose phosphate from hexose and phosphoric acid. Actually, certain chemical conversions can be carried out more efficiently by fermentation than by chemical synthesis.

Many chemical reactions caused by microorganisms are very complex, however, and cannot easily be classified; so the concept of fermentation itself as a chemical conversion has been developed. According to Silcox and Lee,[3] the five basic prerequisites of a good fermentation process are:

1. A microorganism that forms a desired end product. This organism must be readily propagated and be capable of maintaining biological uniformity, thereby giving predictable yields.
2. Economical raw materials for the substrate, e.g., starch or one of several sugars.
3. Acceptable yields.
4. Rapid fermentation.
5. A product that is readily recovered and purified.

According to Lee, certain factors should be stressed in relation to the fermentation chemical-conversion or unit-process concept, such as microorganism, equipment, and the fermentation itself. Certain critical factors of the fermentation are pH, temperature, aeration-agitation, pure-culture fermentation, and uniformity of yields.[4] The microorganisms should be those which flourish under comparatively simple and workable modifications of environmental conditions.

In understanding, hence in correctly handling, microorganisms, a sharp differentiation should usually be made between the initial growth of a selected strain of these organisms to a sufficient quantity and the subsequent processes whereby, either through their continued living or as a result of enzymes previously secreted, the desired chemical is manufactured. To obtain a maximum chemical yield, it is frequently advisable to suppress additional increase in the quantity of the microorganism. Highly specialized microbiologists are engaged in selecting and growing the particular strain of an organism that has been shown to produce the chemical wanted with the greatest yields, the least by-product, and at the lowest cost.

No longer will just any yeast do to make industrial alcohol or a fermented beverage; not only are wild yeasts exlcuded, but a special strain must be used.

The yeasts, bacteria, and molds employed in fermentation require specific environments and foods to ensure their activities. The concentration of the sugar or other food affects the product. The most favorable temperature varies (5 to 40°C), and the pH also has great influence. Indeed, the bacteriologist has developed acid-loving yeasts, so that wild yeasts, not liking acidic conditions, do not flourish. Some microorganisms require air (aerobic), and others go through their life processes without air (anaerobic). Certain anaerobes neither grow nor function in the presence of air. In directing these minute vegetative organisms, conditions can be controlled to encourage the multiplication of the organism first, and then its *functioning*, either directly or through the *enzymes* secreted. How important this is can be seen from the knowledge that to grow 1 g of yeast (dry basis) requires 1.5 to 2.0 g of monosaccharide per day, and 6 g to maintain it. By virtue of this growth, organic catalysts, or *enzymes*, are frequently formed that directly cause the desired chemical change. During the growth period, in addition to the primary, or energy food, such as monosaccharides for yeast,

[3]Silcox and Lee, Fermentation, *Ind. Eng. Chem.* 40 1602 (1948).

[4]Humphrey, Fermentation Technology, *Chem. Eng. Prog.* 73 (5) 85 (1977).

various *nutrients* are needed, such as small amounts of phosphates and nitrogenous compounds, as well as favorable pH and temperature. Finally, certain substances poison these microorganisms and their enzymes. Even the alcohol formed by the yeasts eventually reaches a concentration (varying with the yeast from about 2 to 15%) that will suppress the activity of the organism and its enzymes.

More than 23,000 t/year of antibiotics are produced worldwide.[4a] Other fermentation products produced in large quantities (more than 23,000 t/year) are enzymes, organic acids, solvents, vitamins, and amino acids. The largest volume materials are monosodium glutamate and citric acid.[5]

INDUSTRIAL ALCOHOL

Industrial alcohol was an outgrowth of alcoholic beverages, but now it has become important by virtue of its economically useful properties as a solvent and for synthesis of other chemicals. Alcohol is sold as tax-paid[6] alcohol or, much more widely, as nontaxed denatured alcohol. The completely denatured formulas are admixtures of substances which are difficult to separate from the alcohol and which smell and taste bad, all this being designed to render the alcohol nonpotable. Such completely denatured alcohol is sold widely without bond. Factories find it an essential raw material. A typical completely denatured alcohol formula follows:

To every 100 gal of ethyl alcohol of not less than 160 proof add:
0.125 gal of Pyronate or a compound similar thereto.
0.50 gal of acetaldol (β-hydroxybutyraldehyde), 2.50 gal of methyl isobutyl ketone, and 1.00 gal of kerosene.

The federal government has recognized the needs of industry for alcohol in such form that it can enter into specialized manufacturing processes where the denaturants used in completely denatured alcohol would interfere. Since 1906, when the first U.S. denatured alcohol law was passed, many formulas for specially denatured alcohol have been approved by the federal authorities. Such special formulas are limited to certain designated processes and are manufactured, stored, and used under bond to prevent unlawful consumption. However, the 40 approved special formulas under their authorized uses enter into an exceedingly broad section of the entire industrial life of the nation.[7] These special denatured alcohols are also

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[4a]t = 1000 kg.

[5]ECT, 3d ed., vol. 9, 1980, p. 877.

[6]The federal tax is $10.50 per proof gallon, hence $19.95 on a gallon of 190-proof alcohol. The total sum collected by the federal alcohol tax unit was $5,612,714,948 in 1978, largely from beverages. A *proof gallon* (tax gallon or 3.785 L) signifies a gallon containing 50% alcohol by volume; 100 volumes of 100-proof alcohol contain 50 volumes of absolute alcohol and 53.73 volumes of water owing to volume contraction. Ordinary alcohol of 95% strength is thus 190-proof alcohol, and pure anhydrous alcohol is 200 proof. The lower limit of alcohol dilutions which burn by direct ignition at ordinary temperatures is about 100-proof. A *wine gallon* is a measure of volume (3.785 L) of any proof.

[7]Withdrawals of specially denatured alcohol in 1978 amounted to 222.3×10^6 wine gallons and only 1.14×10^6 wine gallons of completely denatured alcohol.

nonpotable, but the denaturants are easier to remove than those in completely denatured alcohol. Typical specially denatured formulas are:[8]

To every 100 gal of 190-proof ethyl alcohol add:

SD No. 1. Approved wood alcohol, 5 gal. Withdrawals for authorized uses: plastics, dehydrations, explosives, food products, chemicals, etc.

SD No. 2B. Benzene, 0.5 gal. Withdrawals for authorized uses: plastics, dehydrations, explosives, food products, chemicals, etc.

SD No. 29. 100% acetaldehyde, 1 gal, or an alcoholic solution of acetaldehyde (20%), 5 gal. Withdrawals for authorized uses: manufacturing acetaldehyde, acetic acid, esters, ethers, etc.

In industrial nomenclature alcohol means ethyl alcohol, or ethanol (C_2H_5OH). It is sold by the gallon, which weighs 4.082 kg and contains 95% C_2H_5OH and 5% H_2O, both by volume at 15.56°C.[9] No distinction is made concerning the source of the alcohol, i.e., whether from fermentation or from synthesis.

USES AND ECONOMICS. Alcohol is second only to water in solvent value and is employed in nearly all industries. In addition, it is the raw material for making hundreds of chemicals, such as acetaldehyde, ethyl acetate, acetic acid, ethylene dibromide, glycols, ethyl chloride, and all ethyl esters.

The use of fermentation alcohol in motor fuel has been the subject of much controversy.[10] Proponents argue that alcohol, made from renewable, biological materials, can be used to help make the United States less dependent upon foreign sources of petroleum. They also claim it can be used as a method of utilizing much surplus grain and waste biomass materials. In 1980 the U.S. government announced an ambitious program to quadruple the use of alcohol for fuels production to 1.9×10^9 L/year by the end of 1981 and to 42×10^9 L/year by 1990. The goal is to displace 10 percent of the nation's gasoline with gasoline-alcohol fuels (gasohol).

Opponents claim that to produce that much alcohol would require not only using all the surplus grain available but also radically new technology to convert economically wood, cellulose, and other starchy wastes to alcohol. One of the chief difficulties in using alcohol in gasoline is that the usual 95% ethanol is not miscible with gasoline. Only absolute or 99.5% alcohol will mix with gasoline for gasohol; this requires costly extra processing, because simple distillation will not produce ethanol above 95% concentration. Many new methods for lower cost distillation or other ways of removing the water in the alcohol have been proposed, but so far absolute alcohol continues to cost more to produce than gasoline.[11]

At the present time, 1982, ethanol is being used as an octane booster for gasoline, and a small amount is being consumed as gasohol. However, because of government subsidies, the

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[8]*Formulas for Denatured Alcohol*, U.S. Revenue Service, Part 12 of Title 26, Federal Regulations, 1961.

[9]This corresponds to 92.423% of ethyl alcohol by weight. However, when alcohol percentage strength is given, it usually refers to percentage by volume.

[10]Is the U.S. Ethanol Goal Feasible? *Chem. Eng.* 87 (21) 53 (1980); Mendelsohn and Wettstein, Ethanol from Wood, *Chem. Eng.* 88 (12) 62 (1981).

[11]*Chemtech* 11 (12) IBC (1981); *Chem. Eng.* 88 (11) 29 (1981); *Chem. Eng. News* 59 (11) 15 (1981); *Chem. Eng.* 87 (23) 103 (1980); *Chem. Week* 13 (3) 10 (1983); Fong, Jones, and Semrau, Costs of Producing Ethanol from Biomass, *Chem. Eng. Prog.* 76 (9) 39 (1980); Standiford, Energy Conservation in Alcohol Production, *Chem. Eng. Prog.* 79 (1) 35 (1983).

cost of fermentation alcohol is now low enough for it to be competitive with petroleum-based synthetic ethanol. In 1983 the U.S. synthetic alcohol capacity was 8.1×10^8 kg and production was only 4.5×10^8 kg. The price of synthetic ethanol was 61 to 65 cents per kilogram, about the same as that of fermentation ethanol for solvent purposes.[12]

Manufacture

RAW MATERIALS. The manufacture of alcohol from ethylene and other synthetic manufacturing procedures, now the most important source, is discussed in Chap. 38 and illustrated by the flowchart in Fig. 38.9. Alcohol from cellulosic materials, wood, wood wastes, and sulfite liquors, is considered in Chap. 32, principally under wood hydrolysis. This procedure is not competitive except under special conditions, largely because of the cost of converting cellulosic materials to fermentable sugars. Of the 760×10^6 L of industrial ethanol (excluding fuels) produced in the United States in 1981 less than 2 percent was made by fermentation. Continually changing prices of the various carbohydrate feedstocks available can cause major changes in the ratio and it is certainly possible that petroleum shortages will make this process important again as it once was when cheap Cuban molasses was used as the fermentable material. Corn is considered to be the most promising raw material for fermentation to alcohol, especially for gasohol. The yield of 25 kg of corn will be 9 to 11 L of alcohol. Table 4.2 shows the production of ethyl alcohol from various raw materials.

The principal reactions in alcohol fermentation are:

EQUATIONS OF MONOSACCHARIDE PRODUCTION[13]

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

[12]Key Chemicals, *Chem. Eng. News* 59 (45) 14 (1981).

[13]If sugar (sucrose) is fermented it must first be inverted by the enzyme invertase to yield glucose and fructose which can then be converted to alcohol.

***Table* 4.2** 1978 Ethyl Alcohol Production by Type of Raw Materials (thousands of liters of 95% alcohol)

Raw Material	Liters
Ethyl sulfate	1,445,851
Ethylene gas	518,627
Grain and grain products	6,045
Redistillation	11,253
Molasses	78,857
Sulfite liquors	27,842
Whey	125
Total	2,088,600

SOURCE: *Alcohol and Tobacco Summary Statistics*, ATF Publication P1323.1 (4-81), 1978.

EQUATIONS OF FERMENTATION[14]

$$\underset{\text{Monosaccharide}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{Alcohol}}{C_2H_2O_5OH} + 2CO_2 \qquad \Delta H = -130 \text{ kJ}$$

$$\underset{\text{Monosaccharide}}{2C_6H_{12}O_6} + H_2O \rightarrow \underset{\text{Alcohol}}{C_2H_5OH} + \underset{\text{Acetic acid}}{CH_3COOH} + 2CO_2 + \underset{\text{Glycerin}}{2C_3H_8O_3}$$

A small amount of glycerin is always found in alcohol fermentations. Toward the end of a fermentation, the acidity and the glycerin increase.

These are the classic Gay-Lussac equations for alcohol formation. They are the principal equations in an acid or low pH medium. When growing yeast for sale as such or for inoculation, the yield of alcohol is lower, since it is partly changed to CO_2 and H_2O. This fermentation, like so many industrial reactions, is much more involved than these simple reactions indicate. Probably the first step is phosphate hexose ester formation, followed by a split in the six-carbon chain. The fusel oil (mixed amyl alcohols with some propyl, butyl, and hexyl alcohols and esters), amounting to 3 to 11 parts per 1000 parts of alcohol, obtained from yeast fermentations, is thought to be furnished by the protein materials in the mash fermented.

ENERGY REQUIREMENTS, UNIT OPERATIONS, CHEMICAL CONVERSIONS. Plant procedures require steam heating for distillation, power for pumping, and water for condensation, and occasionally for cooling during the exothermic fermentation. Several new methods of handling the various steps with the aim of improving energy efficiency have been proposed.[15] Conventional corn units to produce anhydrous alcohol demand 13 kg of steam per liter of product. Some of the newer processes claim to cut this to 2 kg per liter.

The manufacture of alcohol, as presented in Fig. 4.1, can be broken down into the following steps. The main steps in the competitive manufacture of alcohol from petroleum cracking (cf. Fig. 38.9), are shown in parallel comparisons.

Fermentation Alcohol	Alcohol from Ethylene
Transportation of corn or molasses	Liquefaction of petroleum gases containing ethylene
Storage of corn or molasses	Rectification to produce pure ethylene and pure ethane
Grinding, etc., of corn	Dehydrogenation of ethane to ethylene
Hydrolysis by heating of cornmeal with malt or acid to make mash	Hydration over a catalyst
Growth of inoculating cultures	Distillation of alcohol from partially converted ethylene
Fermentation of diluted inverted molasses or of corn mash	Rectification and purification of alcohol
Distillation of alcohol from "beer"	
Rectification and purification of alcohol	
Recovery of by-products, e.g., CO_2, feed, potash salts	

[14]Prescott and Dunn, *Industrial Microbiology*, 3d ed., chap. 4, McGraw-Hill, New York, 1959; Michaelis, Chemistry of Alcoholic Fermentation, *Ind. Eng. Chem.* 27 1037 (1935).

[15]Low Energy Processes Vie for Ethanol-Plant Market, *Chem. Eng.* 87 (6) 57 (1980).

MAKING OF INDUSTRIAL ALCOHOL.[16] The flowchart in Fig. 4 .1 shows the various operations involved in changing corn to alcohol. The corn is degerminated, dehulled, and milled, either wet or dry. The milled corn is conveyed to the cooker. Cooking is necessary to gelatinize the ground grain so that the barley malt amylases can convert the starch to fermentable sugars. The cookers may be batch or continuous and are operated under pressure. In the continuous process the grain is precooked for 1 to 5 min with water and stillage (the dealcoholized, fermented beer that is discharged from the bottom of the beer still). The mash is continuously fed to a steam heater that instantaneously raises the temperature to 175°C. The mash is passed through a series of pipes and discharged through a relief valve into a flash chamber. Time in the cooker is about 1.5 min and the pressure is maintained at 60 to 100 kPa gage. The temperature of the mash drops to about 60°C in the flash chamber.

The gelatinized (cooked) grain mash is mixed with malted barley and water. The mix is pumped through a pipeline (converter) for 2 min at 60°C and then is sent to the fermentors through pipe coolers. The starch is hydrolyzed to about 70% maltose and 30% dextrins in the short time in the converter. Stillage (20 to 25% of the final mash volume) from the beer still is added to the converted grain mash prior to fermentation to lower the pH, furnish nutrients for the yeast, and to add buffering action.

Meanwhile a charge of the selected yeast (about 5 percent of the total volume) has been growing in the yeast tub on a corn-barley malt mash which has been previously sterilized under pressure and cooled. Bacteriologists have cultivated a strain of yeast that thrives under acid conditions whereas wild yeasts and bacteria do not.

The mash is pumped into the fermentor and the yeast added as soon as 10 percent of the malt has been pumped. The initial pH is adjusted to 4.8 to 5.0 with sulfuric acid and/or stillage. As the reaction indicates, fermentation is exothermic, so cooling may be necessary to ensure that the maximum temperature does not exceed 32°C. The time of the fermentation cycle may vary from 40 to 72 h.

The liquors in the fermentors, after the action is finished, are called *beer.*[17] The alcohol is separated by distillation. The beer, containing from 6.5 to 11% alcohol by volume, is pumped

[16]Underkofler, *Industrial Fermentations*, vol. I, Chem. Publ. Co., New York, 1954.

[17]This is a general term applied to the result of any such fermentation, whether it results finally in industrial alcohol or the beverage beer, or whiskey, or butyl alcohol and acetone; ECT, 3d ed., vol. 9, 1980, p. 355.

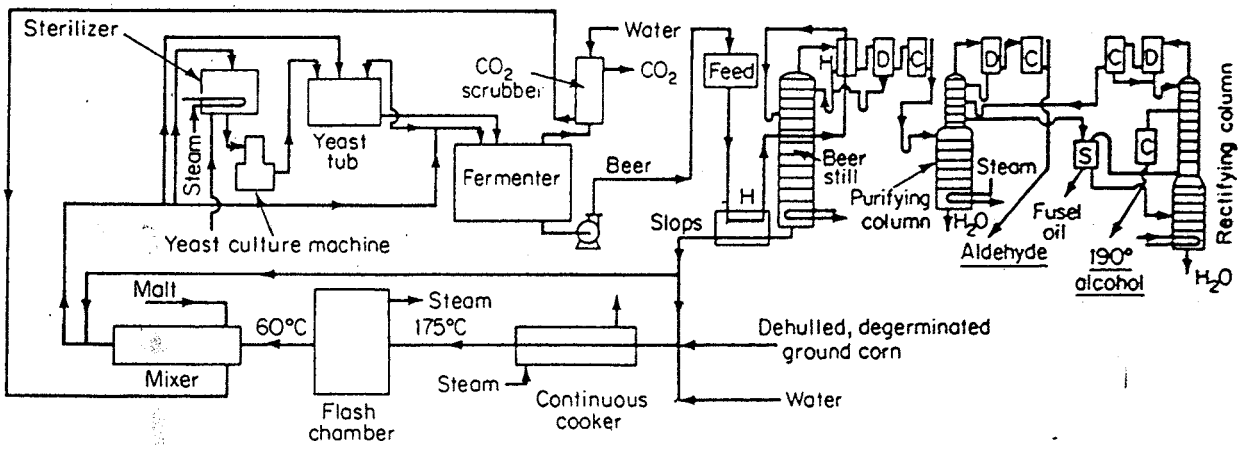


Fig. 4 .1. Flowsheet for industrial alcohol. KEY: C, condensor; D, dephlegmator; H, heat exchanger; S, separator.

to the upper sections of the beer still, after passing several heat exchangers. As the beer passes down the column, it gradually loses its lighter boiling constituents. The liquid discharged from the bottom of the still through a heat exchanger is known as *stillage*. It carries proteins, residual sugars, and in some instances, vitamin products so it is frequently evaporated and used as a constituent of animal feed. The overhead containing alcohol, water, and aldehydes passes through a heat exchanger to the partial condenser, or dephlegmator, which condenses sufficient of the vapors to afford a reflux and also to strengthen the vapors that pass through to the condenser, where about 50% alcohol, containing volatiles, or aldehydes, is condensed. This condensate, frequently known as the high wines, is conducted into the aldehyde, or heads, column, from which the low-boiling impurities are separated as an overhead. The effluent liquor from part way down the aldehyde column flows into the rectifying column.

In this third column the alcohol is brought to strength and finally purified in the following manner: The overhead passing through a dephlegmator is partly condensed to keep the stronger alcohol in this column and to provide reflux for the upper plates. The more volatile products, which may still contain a trace of aldehydes and of course alcohol, are totally condensed and carried back to the upper part of the aldehyde still. Near the top of the column 95 to 95.6% alcohol is taken off through a condenser for storage and sale. Farther down the column, the higher boiling fusel oils are run off through a cooler and separator to a special still, where they are rectified from any alcohol they may carry before being sold as an impure amyl alcohol for solvent purposes. The bottom of this rectifying column discharges water.

Alcohol-water mixtures are rectified to increase the strength of the alcohol component by virtue of the composition of the vapors being stronger in the more volatile constituent than the liquid from which these vapors arise. This is shown quantitatively by the curves in Fig. 4.2, where the composition of the vapor in equilibrium with the liquid is on a horizontal line. However, alcohol cannot be made stronger than 95.6% by rectification, because, as can be seen from Fig. 4.2, water forms a binary constant-boiling mixture of this composition which boils slightly lower than absolute, or anhydrous, alcohol. The principles shown here are the basis of the strengthening of the more volatile constituent of any liquid mixture by distillation.

ABSOLUTE ALCOHOL[18]

Anhydrous alcohol was formerly made by absorbing the 4 to 5% water present in 95 to 96% industrial alcohol using quicklime, with subsequent distillation. This process was expensive, and although it produced a very high quality of anhydrous alcohol, it has now been superseded. Ethyl alcohol and water form an azeotrope which is 95% by volume alcohol. Various methods are in use and/or have been suggested for removing the last 5% of water to produce 100% alcohol. Table 4.3 lists a number of separation routes and also shows the energy necessary to accomplish the water removal.

The oldest method is distillation of the 95% azeotrope using a third component which forms a minimum constant-boiling mixture boiling at a lower temperature than the 95% alcohol or

[18]This is practically 100% ethyl alcohol, frequently known as *absolute* alcohol, but since the absence of water is more notable than that of other impurities, the term *anhydrous* is preferred by some.

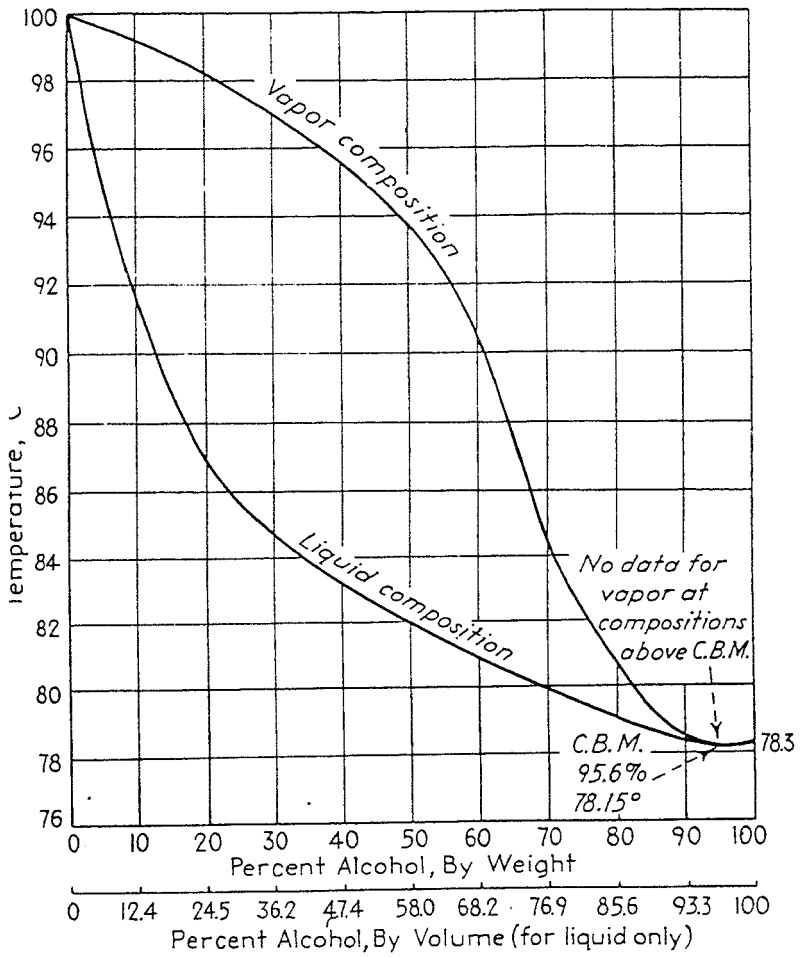


Fig. 4.2. Temperature versus composition of vapor and liquid for alcohol-water at 101 kPa.

the water. Figure 4.3 shows the three binary minimum constant-boiling mixtures in the system, using benzene as the third component (entrainer), as well as two homogeneous mixtures, a heterogeneous (water and benzene) one, and a ternary one. The ternary mixture is the lowest-boiling composition in the system, boiling at 64.85°C as shown at point F. The starting composition of the mixture must lie on the straight line CF to ensure that removal of the constant-boiling mixture will leave anhydrous alcohol in the still. If the starting mixture is made up by adding benzene to 95% alcohol, the starting composition must also lie along the line EB. Therefore, the intersection G represents the starting composition. If enough benzene is added to 95% alcohol to bring the total composition to point G, continuous distillation gives the ternary constant-boiling mixture (bp 64.85°C) at the top of the column and absolute alcohol (bp 78.3°C) at the bottom of the column.

An important feature[19] of the process is separation of the condensate into two liquid layers, represented in Fig. 31.3 by points M and N. The ratio of the top layer N to the bottom layer M is equal to MF/FN, or 84:16. The compositions involved are shown in Fig. 4.4, which also illustrates how this process functions. These same principles of distillation in multicomponent systems, involving various constant-boiling mixtures, are used for dehydrating other

[19]Guinot and Clark, Azeotropic Distillation in Industry, *Trans. AIChE* (London) 16 189 (1938).

Table 4.3 Separation Routes to Absolute Alcohol

Type of Separation	Ethanol, % Initial	Ethanol, % Final	Process	Energy Needed, kJ/L
Complete	10	100	Conventional "dual" distillation	7600
Complete	10	100	Extraction with CO_2	2200–2800
Complete	10	100	Solvent extraction	1000[a]
Complete	10	100	Vacuum distillation	9800[b]
To azeotrope	10	95	Conventional distillation	5000
To azeotrope	10	95	Vapor recompression	1800[a]
To azeotrope	10	95	"Multieffect" vacuum	2000[c]
Azeotropic	95	100	Conventional azeotropic distillation	2600
Azeotropic	95	100	Dehydration via adsorption	335[d]
Azeotropic	95	100	Low-temperature blending with gasoline	800[e]
Azeotropic	95	100	Molecular sieve	1300–1750
Other	3	10	Reverse osmosis	140

[a]Figure given is the thermal energy required to provide mechanical energy for the process.

[b]For single-column distillation.

[c]For three-column distillation.

[d] For drying with CaO; energy requirements using fermentable grains would be considerably less.

[e]Results directly in production of gasohol.

SOURCE: Battelle Pacific Northwest Laboratories, *Chem. Eng.* 88 (11) 29 (1981).

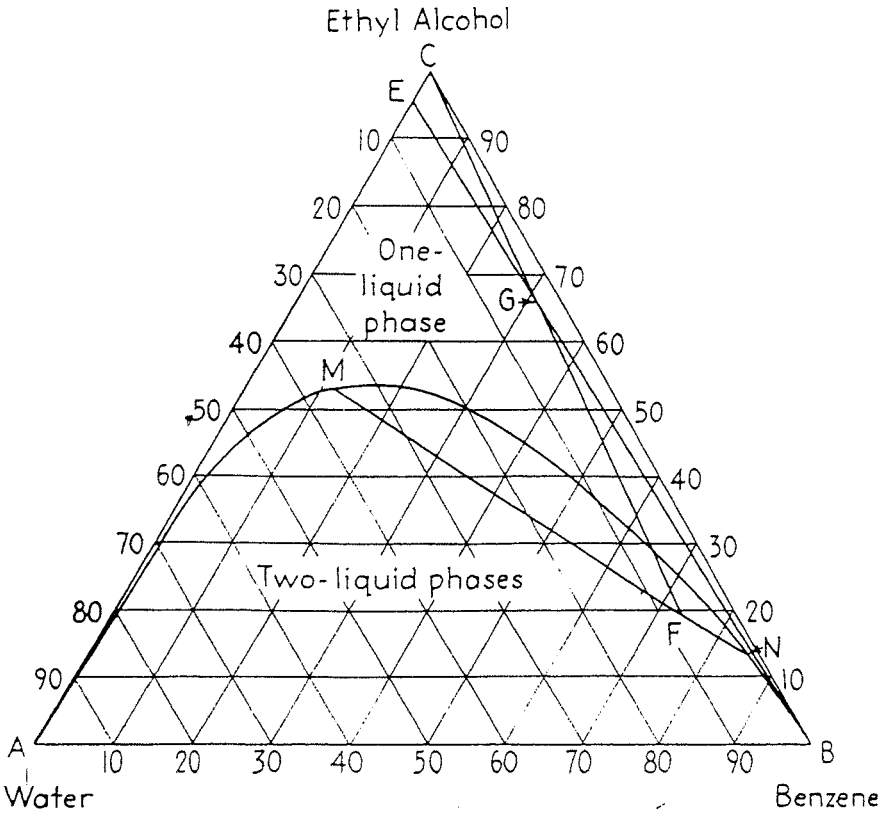
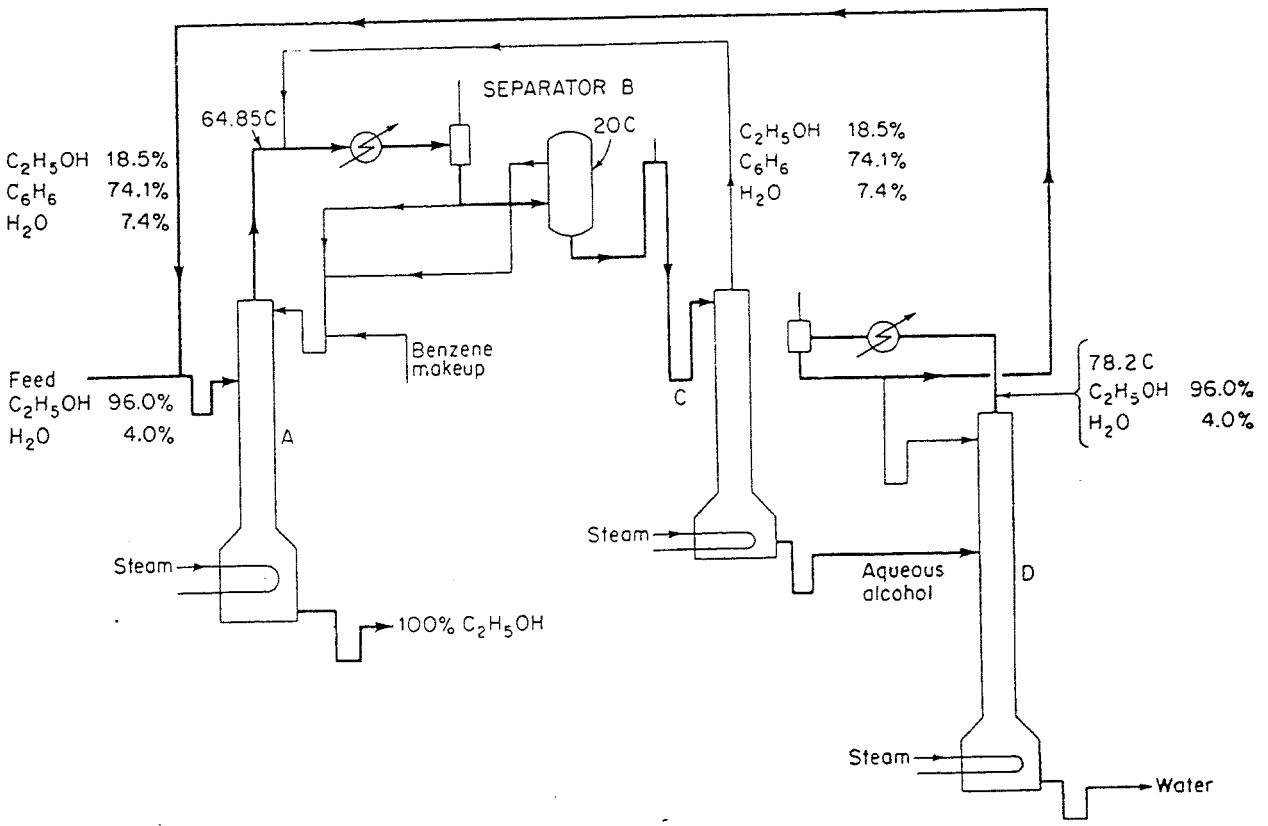


Fig. 4.3. Ternary diagram of the liquid system water-alcohol-benzene.



	TOP LAYER	BOTTOM LAYER
	SEPARATOR EQUILIBRIUM	
Vol. % overhead	84.0	16.0
	COMPOSITIONS, %	
C_2H_5OH	14.5	53.0
C_6H_6	84.5	11.0
H_2O	1.0	36.0

Fig. 4.4. Dehydration of 96% ethanol to absolute alcohol by azeotrope distillation with benzene at 101 kPa. Column A has 95% alcohol fed into it. The ternary azeotrope is taken overhead in this column, and absolute alcohol is obtained as a bottoms product. The overhead vapors are condensed and passed to separator (decanter) B, in which two liquid layers form. The upper layer, rich in benzene, is returned to column A as reflux, and the lower layer is fed to column C which produces the ternary azeotrope as the overhead product and benzene-free aqueous alcohol as the bottoms product. This latter product is fed to column D which produces by ordinary distillation an overhead product of 95% alcohol and a bottoms product of nearly pure water. The benzene is recycled continuously in this system, and it is necessary only to make up the benzene losses from the system. This withdrawing agent is used over and over again with a loss that should not exceed 0.5 percent of the volume of the anhydrous alcohol produced. [*Perry, p. 13-42; Chem. Eng.* 67 *(10) 129 (1960).*]

organic liquids, such as propyl alcohol and for removing the water formed in sulfonations (benzenesulfonic acid) and esterifications (ethyl acetate).[20] The fundamentals of distillation are presented because of the extensive data on alcohol that are available.

The data in Table 4.3 clearly show that this conventional "dual" distillation process requires much more energy than any of the other possible methods of removing the last water in the alcohol, with the exception of vacuum distillation. One of the newer proposals is to use cellulose or cornmeal to adsorb the water. Aluminum oxide and silicon oxide adsorbents have also been used. Another promising method is to use liquid CO_2 to extract the ethanol and then depressurizing to flash off CO_2. Other solvents, such as dibutyl phthalate, which are immiscible with water but are good solvents for ethanol, are under investigation.

Interest in cutting energy demand for production of 100% alcohol is very great because of the proposed use of gasohol.[21] The energy liberated by burning 1 L of 100% alcohol is about 23 MJ and thus, because many of the present processes for fermenting and distilling corn-derived alcohol consume up to 42 MJ/L, the energy consumed in preparing the alcohol is greater than its potential energy content. To make gasohol a viable economic product will require processes that can produce it with much smaller amounts of energy than have been used in the past. The average total energy consumption for the new processes is 11 to 12.5 MJ/L; several of the processes claim much lower energy demands.

BEERS, WINES, AND LIQUORS

The making of fermented beverages was discovered by primitive humans and has been practiced as an art for thousands of years. Within the past century and a half it has evolved into a highly developed science. A good brewer has to be an engineer, a chemist, and a bacteriologist. In common with other food industries, the factors taste, odor, and individual preference exist to force the manufacturer to exert the greatest skill and experience in producing palatable beverages of great variety. In the last analysis, the criterion of quality, with all the refinements of modern science, still lies in the human sensory organs of taste, smell, and sight.

Alcoholic beverages are divided into three groups: malt liquors, fermented wines, and distilled liquors. Beer and ale require malted (germinated) grain to make the carbohydrates fermentable, wines are produced by the action of yeast on the sugar of fruit, and distilled liquors are fermented liquors which are then distilled to increase the alcoholic content.

USES AND ECONOMICS. As Table 4.4 indicates, many millions of gallons of alcoholic beverages are manufactured in the United States each year. The amount of wine production has been increasing rapidly in recent years. In 1981[22] the consumption of malt beverages was 95.8 L, wine and brandy, 8.7 L, and distilled spirits, 11 L, all per capita (adult).

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[20]Hoffman, *Azeotropic and Extractive Distillation*, Interscience, New York, 1964.

[21]Black, Distillation Modeling of Ethanol Recovery and Dehydration Processes for Ethanol and Gasohol, *Chem. Eng. Prog.* 76 (9) 78 (1980); Low Energy Processes Vie for Ethanol-Plant Market, *Chem. Eng.* 87 (6) 57 (1980); *Chem. Eng.* 88 (19) (1981); Lowering the Cost of Alcohol, *Science*, 206 October 5, 1979, p. 641.

[22]*U.S. Industrial Outlook, 1982*, U.S. Department of Commerce.

***Table* 4.4** U.S. Production of Alcoholic Beverages, 1965–1978 (in thousands)

Beverage	1965	1972	1978
Sparkling wine, wine gal	6,358	22,864	23,808
Still wine, wine gal	197,257	366,189	473,074
Rectified, proof gallon	92,923	120,815	114,836
Beer, barrel*	108,015	140,327	176,347

*1 barrel equals 31 gal or 117 L.

SOURCE: *Alcohol and Tobacco Summary Statistics*, ATF Publication P1323.1 (4-81), 1978.

RAW MATERIALS. Grains and fruits supplying carbohydrates are the basic raw materials. The variety of grains and fruits employed is wide, changing from country to country, or from beverage to beverage. Russia ferments potatoes and by distillation obtains vodka; similar treatment of the sap of the maguey in Mexico yields pulque; but the world's chief raw materials for fermentations are the cereals, corn, barley, and rice, and grapes.

Beer[23]

Beer and allied products are beverages of low alcoholic content (2 to 7%) made by brewing various cereals with hops, usually added to impart a more-or-less bitter taste and to control the fermentation that follows. The cereals employed are barley, malted to develop the necessary enzymes and the desired flavor, as well as malt adjuncts such as flaked rice, oats, and corn; wheat is used in Germany, and rice and millet in China. Brewing sugars and syrups (corn sugar, or glucose) and yeast complete the raw materials. For beer the most important cereal is barley, which is converted into malt by partial germination. Most brewers buy finished malt from suppliers rather than making their own.

To make malt the barley is steeped in cold water and spread out on floors or in special compartments and regularly turned over for from 5 to 8 days, the layers being gradually thinned as the germination proceeds. At the proper time, when the enzymes are formed, growth is arrested by heat. During growth, oxygen is absorbed, carbon dioxide is given off, and the enzyme diastase is formed. This enzyme is the biological catalyst that changes the dissolved starch into the disaccharide maltose which, after transformation into the monosaccharide glucose by maltase, is directly fermentable by yeast.

The flowchart for beer manufacture in Fig. 4.5 may be divided into three groups of procedures: (1) brewing of the mash through to the cooled hopped wort, (2) fermentation, and (3) storage, finishing, and packaging for market. Mashing is the extraction of the valuable constituents of malt, malt adjuncts, and sugars by macerating the ground materials with 190 to 230 L of water per 100 kg of materials listed in Fig. 4.5 and treating with water to prevent too high a pH, which would tend to make a dark beer. In the pressure cooker, the insoluble

[23]Urang, Debating the Draft, *Chem. Bus.*, May 4, 1981, p. 29. ECT, 3d ed., vol. 3, 1978, pp. 692–735; Marchall et al., Enzymes in Brewing, *Brew. Dig.* 57 (9) 14 (1982); Peppler and Perlman (eds.), *Microbial Technology*, 2d ed., vol. II. Academic, New York, 1979.

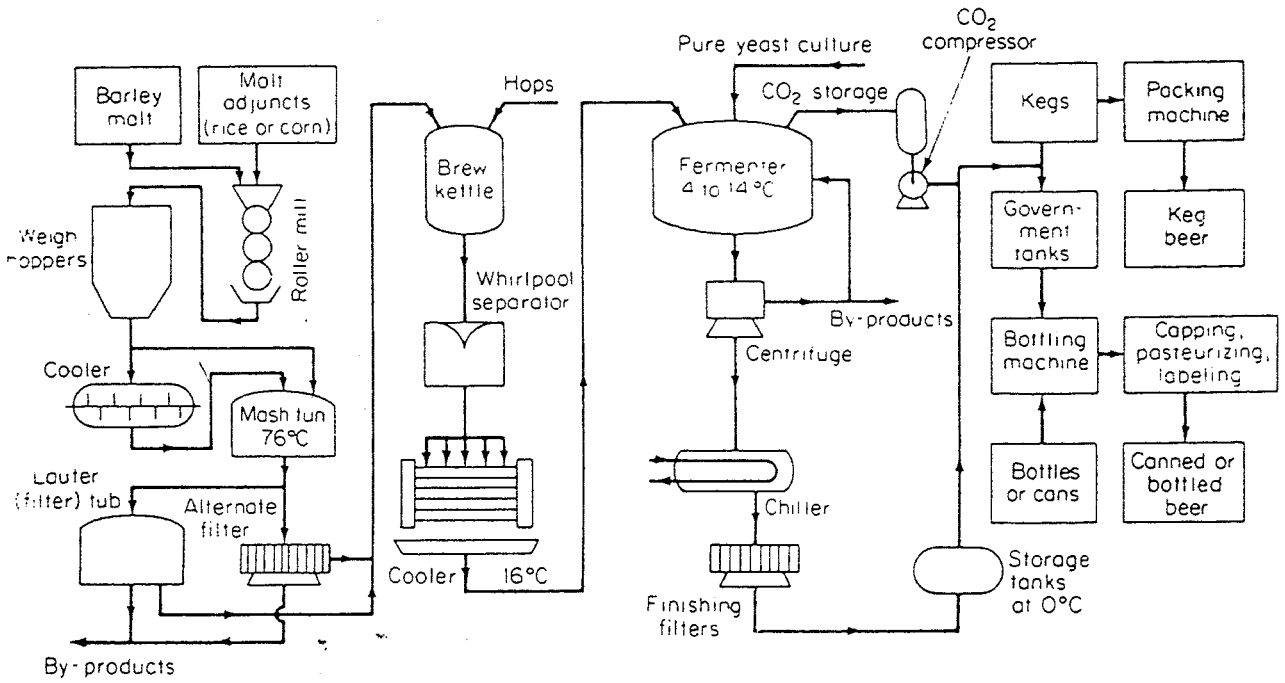

Fig. 4.5. Flowchart for the production of beer

starch is converted into liquefied starch, and the soluble malt starch into dextrin and malt sugars. The resulting boiling cooker mash, mixed with the rest of the malt in the mash tub, which raises the temperature to 75°C, is used to prepare the brewers' wort.[24] This is carried out in the mash tub. After all the required ingredients have been dissolved from the brewing materials, the entire mash is run from the mash tub to filter presses or the lauter or straining tub, where the wort is separated from the insoluble spent grains through a slotted false bottom and run into the copper wort cooker. For complete recovery of all substances in solution, a spray of decarbonated water at 74°C is rained through the grains. This is called sparging.

The wort is cooked for approximately 1 to 1.5 h, during part of which it is in contact with hops. The purpose of boiling is to concentrate the wort to the desired strength, to sterilize it (15 min) and destroy all the enzymes, to coagulate certain proteins by heat (82°C), to modify its malty odor, and to extract the hop resins' tannin and aroma from the hops, which are added during the cooking process. At the end of the time the spent hops are separated from the boiling wort very quickly in a whirlpool separator. Since the spent hops retain 770 L of wort per 100 kg of hops, they should also be sparged. The wort is then ready to be cooled.

The cooling step is not only to reduce the temperature but also to allow the wort to absorb enough air to facilitate the start of fermentation. The wort is then cooled in a plate heat exchanger to 48°C and then aerated. Slight concentration, due to evaporation, occurs. This operation is performed under controlled conditions to prevent contamination by *wild* yeasts. Frequently, sterilized air is used.

The cooled wort is mixed with selected yeasts in the line leading to the starting tubs, between 285 to 380 g of yeast being used per 100 L of beer. The initial fermentation temperature is 4 to 6°C but, as the fermentation proceeds, the temperature rises to 14°C. This is easily explained by the fact that the conversion of the sugar to carbon dioxide and ethyl

[24]The wort is the liquid resulting from the mashing process, i.e., the extracting and solubilizing of the malt and malt adjuncts. Wort composition varies from 17 to 24% solids by weight for the first wort to approximately 1% solids for the last wort removed by the sparge water.

ɔohol by the enzymes of the yeast generate 650 kJ per kilogram of maltose converted. The ɪperature is partly controlled by coolers inserted in the fermentors. The mixture is immed to remove the foreign substances that the evolved carbon dioxide brings to the top. ɪe carbon dioxide evolved is collected by using closed fermentors and is stored under 17,000 'a of pressure for subsequent use in carbonating the beer.

The yeast gradually settles to the bottom of the fermenting tanks in about 7 to 10 days. ɪe liquid is very opalescent in appearance, under a cover of foam. As the beer leaves the rmentors, it contains in suspension hop resins, insoluble nitrogenous substances, and a fair ɪount of yeast. It is then sent to the lagering (aging) tanks where, usually, a second fermentation occurs. The temperature is kept high enough to initiate the second fermentation ɪd then is cooled to 0 to 2°C to lager the beer. Lagering consists of storing at 0 to 2°C for to 4 months. During this time the taste and aroma are improved, and tannins, proteins, and ɔp resins are removed by settling. Highly hopped beers require more lagering time than ɛrs containing less hops. Near the end of the period the beer is saturated with CO_2 at 50 to) kPa.[25] In the United States, public demand favors a brilliant beverage, so the beer is filtered rough a pulp filter under CO_2. About 92 L of beer is produced per 100 L of wort in the ɑrting tubs. After bottling, the beer is pasteurized at 60°C.

Draft beer is not pasteurized. Some bottled beer is not either; it is filtered through fine embranes which remove residual yeast cells and harmful bacteria. This ultrafiltration proɪces so-called bottled draft beer. Light beer has a carbohydrate content of near zero comɑred with the usual 4%. This reduces the food content from 600 kJ to about 420 kJ per 355-l bottle. During fermentation the enzyme glucoamylase is added which converts the nonɛrmentable carbohydrates to glucose. This glucose is then fermented to ethanol.

Beer making has not changed much over the years as brewmasters have been afraid of ɲanging their beer's taste. However, some new plants have installed automatic wort proɯction using hop pellets and using a whirlpool to separate out the hops and sludge. Another ɪnovation which is claimed not to change the final product is high-density brewing wherein ɪe wort is produced with much less water than usual. This means production can be ɪcreased without increasing equipment. The extra water is added after the preliminary fɨation. A universal refrigerant-cooled tank to ferment, age, and finish beer in a single tank ɑs also been developed.

Beer contains about 90% water and can be concentrated (dehydrated) to about one-fourth f its original volume. Ice crystals form below the freezing point of water and can be sepaɑted from the beer concentrate. To reconstitute the beer, water and carbon dioxide ɑre ɗdded.

Vine

Vine has been made for several thousand years by fermentation of the juice of the grape ɔike other fermentations, many primitive procedures have been supplanted by improved cience and engineering to reduce costs and to make more uniform products. But now as lways, the quality of the product is largely related to grape, soil, and sun, resulting in a 'ariation in flavor, bouquet, and aroma. The color depends largely upon the nature of the ɡrapes and whether the skins are pressed out before fermentation. Wines are classified as ɪatural (alcohol 7 to 14%), fortified (alcohol 14 to 30%), sweet or dry, still or sparkling. For-

[25]The carbon dioxide should be kept free from air, which would interfere with the stability ɪnd quality of the beer. The gas is pumped in close to 0°C and amounts to between 0.36 and).45% of the weight of the beer.

tified wines have alcohol or brandy added. In the sweet wines some of the sugar remains unfermented.

For the manufacture of dry red wine, red or black grapes are necessary. The grapes are run through a crusher, which macerates them but does not crush the seeds, and also removes part of the stems. The resulting pulp, or must, is pumped into 11,000- to 38,000-L tanks,[26] where sulfurous acid[27] is added to check the growth of wild yeast. An active culture of selected and cultivated yeast equal to 3 to 5 percent of the volume of juice is added. During fermentation, the temperature rises, so that cooling coils are necessary to maintain a temperature below 30°C. The carbon dioxide evolved carries the stems and seeds to the top, which is partly prevented by a grating floated in the vat. This allows extraction of the color and the tannin from the skins and seeds. When the fermentation slows up, the juice is pumped out of the bottom of the vat and back over the top. The wine is finally run into closed tanks in the storage cellar, where, during a period of 2 or 3 weeks, the yeast ferments the remainder of the sugar. The wine is given a cellar treatment to clear it, improve the taste, and decrease the time of aging. During this treatment the wine is first allowed to remain quiet for 6 weeks to remove part of the matter in suspension, and then racked for clarification.[28] Bentonite, or other diatomaceous earth, may be used for clearing, 20 to 185 g being stirred into every 100 L of wine. An insoluble precipitate with the tannin is also formed. Extra tannin may also be added, and the wine racked and filtered through diatomaceous earth, asbestos, or paper pulp. The wine is corrected to commercial standards by blending it with other wines and by the addition of sugar, acids, or tannins. It is standard procedure to chill some wines for the removal of argols or crude potassium acid tartate, which constitute the commercial source of tartaric acid and its compounds. This treatment also gives a more stable finished wine. By quick-aging methods it is possible to produce a good sweet wine in 4 months. These methods include pasteurization, refrigeration, sunlight, ultraviolet light, ozone, agitation, and aeration. The wine may be held at about freezing for 3 weeks to a month, and a small amount of oxygen gas bubbled in. Then the wine is racked, clarified, and further filtered in the usual manner. The wine trade is large and growing rapidly in the United States.

Distilled Spirits

Various fermented products, upon distillation and aging, yield distilled liquors. Figure 4.6 shows the flowchart for whiskey and gin, and Table 4.5 presents statistics. Brandy is distilled from wine or from the *marc*, which is the pulp left by racking or straining. Making a beer[29] from a grain mixture containing at least 51% corn and distilling and aging it yields bourbon

[26]In many modern American wineries these tanks are even larger and are constructed of concrete.

[27]Potassium or sodium metabisulfite and/or sodium bisulfite may also be used.

[28]During this and the following period the new wine undergoes a complicated series of reactions, resulting in the removal of undesired constituents and development of the aroma, bouquet, and taste. Oxidation takes place, as well as precipitation of proteins and argols, and esterification of the acids by alcohols. Certain modifications of this process are presented in Chemical Technology, Key to Better Wines, *Chem. Eng. News* 51 (27) 44 (1973); Chemistry Concentrates on the Grape, *Chem. Eng. News* 51 (26) 16 (1973).

[29]The yeast in this fermentation is grown in the presence of lactic acid to ensure proper strain and to secure the desired quality of the whiskey

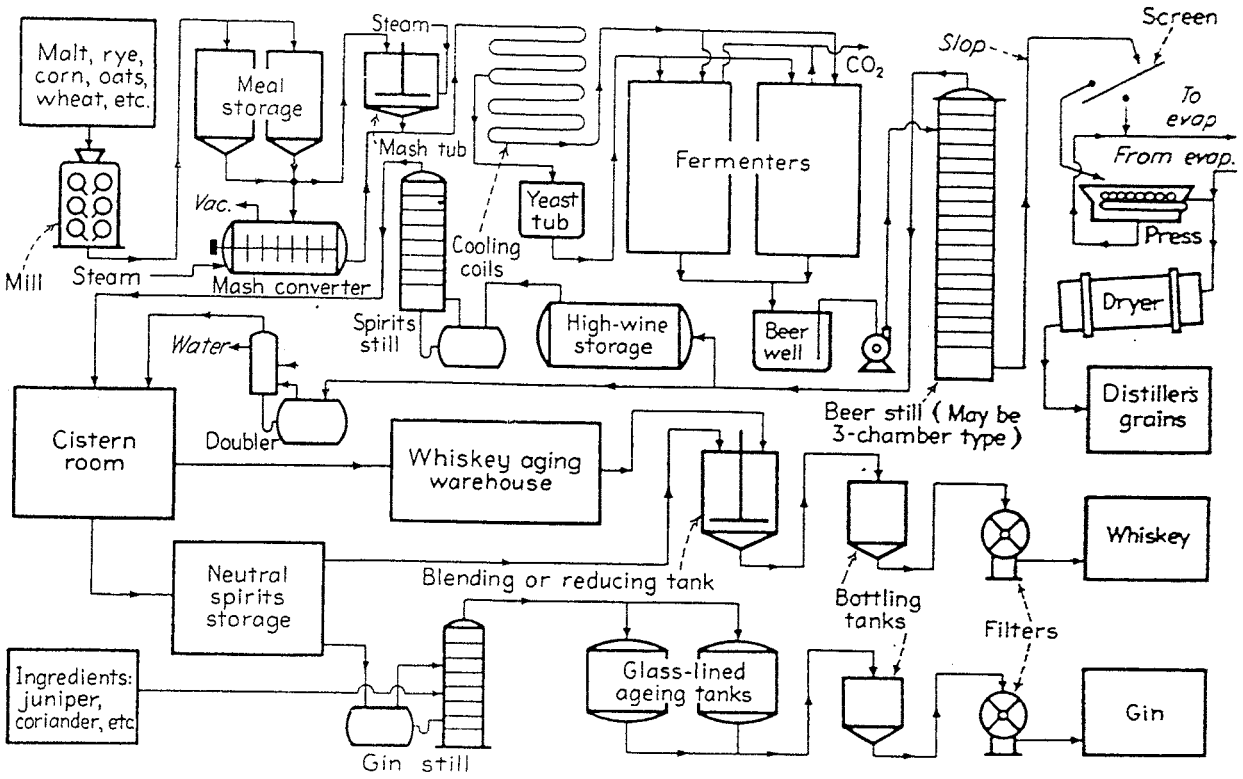

Fig. 4.6. Flowchart for the production of distilled liquors.

whiskey. Similarly, rye whiskey must start with 51% rye in the grain to be mashed and fermented. Scotch whisky (never spelled with an "e" as in all other whiskey) comes only from Scotland and uses barley dried with peat which gives it its distinctive flavor. By inspecting the flowchart in Fig. 4.6 in the light of Fig. 4.1 and 4.5, and the description accompanying them, the procedures in Fig. 4.6 for distilled liquors will be clear. In modern liquor plants the equipment, up to the stills, is of steel, and the stills are of copper or stainless steel. By law, the aging of bourbon or rye whiskey of claimed age must take place in charred new white-oak barrels of approximately 190 L. These are kept in bonded warehouses at 18 to 30°C and at a preferred humidity of 65 to 70%, usually for 1 to 5 years. During this time evaporation of the contents takes place, largely through the ends of the barrel staves. By reason of more

***Table* 4.5** U.S. Net Production of Distilled Spirits (in thousands of proof gallons)

	1970	1975	1980
Whiskey	112,882	140,818	103,860
Brandy	12,353	15,176	14,635
Rum	617	5,594	20,311
Gin	26,922	28,822	24,583
Vodka	20,079	33,483	26,958
Spirits	85,639	83,580	97,519
Total	258,441	307,472	287,864

SOURCE: *Annual Statistical Review, 1980,* Distilled Spirits Industry: Distilled Spirits Council of the United States.

rapid capillary travel and osmosis of the smaller water molecules in comparison with the alcohol molecules, an increase in the percentage of alcohol is found in the barrel contents The government shrinkage allowance is approximately 8 percent the first year, 4 percent the second year, 4 percent the third year, and 3 percent the fourth year. If the shrinkages are exceeded (and this is often the case), the manufacturer must pay a tax on the excess, but with the best cooperages under the best conditions these allowances can just be met. The distillate from the spirit still is under 160 proof and is subsequently diluted upon barreling to 100 to 110 proof. It is not pure alcohol but contains small amounts of many different constituents, generally classed together as congenerics, which by their reaction with each other or the alcohol, or by their absorption, both catalyzed by the char of the wood, help greatly in imparting the whiskey flavor and bouquet. The aging whiskey also extracts color and other products from the charred white oak. Changes of a like nature occur similarly in aging brandy and rum. Here, as in other divisions of the fermentation industries, skill and scientific knowledge aid in the production of a palatable product. By law, whiskey must be fermented from whole grains, so that the germs (containing the corn oil) and the husks are suspended in the liquor from the beer still in whiskey manufacture. This discharge liquor is known as slop, or stillage. As shown in Fig. **4**.6, it is treated to recover the values by separating the solids from the liquid slop. After vacuum evaporation of the liquid portion, it is added to the solids, and the mixture is dried in rotating steam-heated dryers to produce distillers' grains, a valuable cattle feed.

BUTYL ALCOHOL AND ACETONE

Until World War I, all the acetone produced was made by the dry distillation of calcium acetate from pyroligneous acid. Under the stimulus of the wartime demand for acetone for the manufacture of smokeless powder, Weizmann[30] developed a process utilizing the fermentation of starch-containing grains to yield acetone and butyl alcohol. Commercial Solvents Corp. was organized, and it built and operated two plants in the Corn Belt to ferment corn, using *Clostridium acetobutylicum* bacteria. This fermentation, however, gave 2 parts butyl alcohol to 1 part acetone and, until the development of fast-drying nitrocellulose lacquers, particularly for the automotive industry, there was virtually no market for the butyl alcohol produced. Then conditions became reversed, butyl alcohol becoming the important commodity and acetone the by-product. This better sale of first one product and then another is characteristic of industries in the chemical field, where more than one substance results from a process and reflects the changing demand that accompanies a growing and dynamic industry. New cultures feeding on molasses were developed, which also gave a more desirable solvent ratio (approximately 3 parts butyl alcohol to 1 part acetone). Higher costs for molasses and grain now have given the synthetic processes such a dominant position that the latter fermentation process has stopped. Today, acetone is coproduced with phenol by the oxidation of cumene or dehydrogenation of isopropyl alcohol. It is used as a solvent and in fabricating plastics. About 1×10^9 kg was produced in the United States in 1981.[31]

RIBOFLAVIN. Riboflavin was first produced commercially as a by-product of acetone–butyl alcohol fermentation, but the concentration was low. Several greatly improved biological processes have been dominated by the lower-cost synthetic process presently used

[30]Brit. Patent 4845 (1915); U.S. Patent 1,315,585.

[31]*Chem. Eng. News*, 59 (15), 12 (1981).

VINEGAR AND ACETIC ACID

The aerobic bacterial oxidation (by the genus *Acetobacter*) of alcohol to dilute acetic acid (8%) is another ancient procedure, furnishing vinegar, a flavored acetic acid solution, fermented from wine, cider, malt, or dilute alcohol. If pure dilute alcohol is fermented, pure dilute acetic acid results. The yield is 80 to 90% of theory. Air[32] must be supplied, as these formulations indicate:

$$2C_2H_5OH + O_2 \rightarrow 2CH_3CHO + 2H_2O \quad 2CH_3CHO + O_2 \rightarrow 2CH_3COOH$$

Since these reactions are exothermic, either the alcohol can be slowly trickled through the apparatus, letting the heat dissipate, or it can be recirculated with special cooling. If cider, malt, or wine is fermented, the acetic acid content of the resulting vinegar rarely exceeds 5% because of limitations of the sugar content; if dilute alcohol is the raw material, the acetic acid may rise to 12 or 14% at which acidity the bacteria cease to thrive. If a fruit juice is turned to vinegar, certain esters are formed, varying with the raw material and thus imparting a characteristic flavor. Synthetic acetic acid is made from ethylene, or by treating methanol with carbon monoxide.

CITRIC ACID

Citric acid is one of our most versatile organic acids. Its major use is as an acidulant in carbonated beverages, jams, jellies, and other foodstuffs. Another large outlet is in the medicinal field, including the manufacture of citrates and effervescent salts. Industrial uses, relatively small, include citric acid as an ion-sequestering agent buffer and acetyl tributyl citrate, a vinyl resin plasticizer. Citric acid is meeting competition from other organic acids, for example, fumaric, maleic, and adipic.

Except for small amounts (less than 7 percent) produced from citrus-fruit wastes, citric acid is manufactured[33] by aerobic fermentation of crude sugar or corn sugar by a special strain of *Aspergillus niger*, following the classical research by Currie. The overall reactions are

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O + 3O_2 \rightarrow 2C_6H_8O_7 + 4H_2O$$

$$\underset{\text{Dextrose}}{C_6H_{12}O_6} + 1\tfrac{1}{2}\,O_2 \rightarrow \underset{\text{Citric acid}}{C_6H_8O_7} + 2H_2O$$

The fermentation changes sugar and dextrose, straight-chain compounds, into branched chains. An earlier shallow-tray fermentation process was abandoned because of the expensive manual processing and the development of the submerged process.

The submerged process for the manufacture of citric acid is depicted in Fig. 4.7, and this

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[32]Too much air causes losses because of further and undesired oxidation; ECT, 3d ed., vol. 6, 1979, pp. 150–173.

[33]Currie, The Citric Acid Fermentation of *A. niger*, *J. Biol. Chem.* 31 15 (1917).

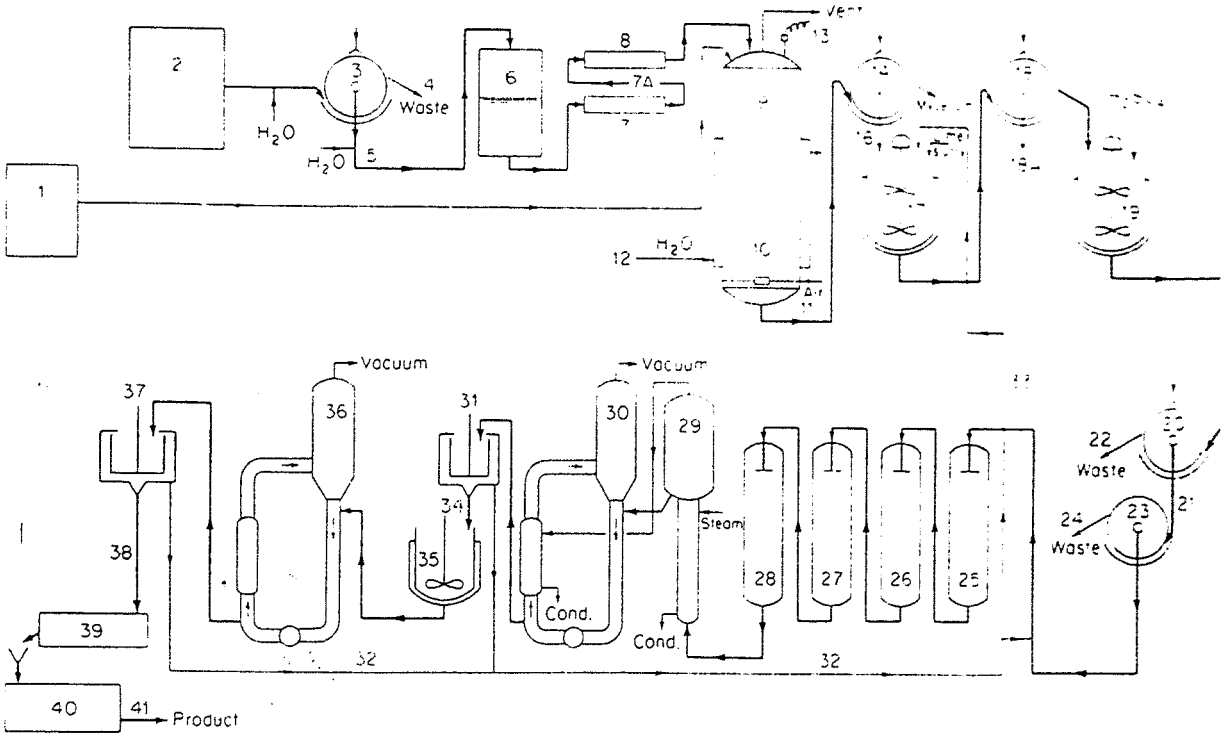

Fig. 4.7. Flowchart for citric acid production. The purification of the dextrose glucose syrup is fundamental (nos. 2 through 8), involving a rotary vacuum filter (3) to remove suspended or precipitated solids after partial dilution. This is followed by a cation-exchange cell (6) for trace-element reduction and a flash pasteurization heater (7), holding loop (7a), and syrup cooler (8). The syrup is pumped into the fermentor (9) plus inoculum (1). The pH adjustment is made and nutrients added. Sterile air (11) from filters and flowmeters is sparged (10) into the fermentor (9). The fermentation process for the production of citric acid is, in its simplest terms, the conversion of a molecule of a hexose sugar to a six-carbon molecule of citric acid (9). The purification and recovery of the resultant acid are then basically an application of the lime-sulfuric scheme first used by Scheele in 1784. Today's methods involve first separating off the mycelium (14) from the broth, which contains the citric acid (16), liming it with milk-of-lime slurry (17), filtering off and washing the resultant calcium citrate (18), and finally decomposing the citrate with sulfuric acid (19). The calcium sulfate formed from this decomposition is filtered off as a waste by-product (20, 23). The more modern plants of today perform these three filtrations on some form of rotary vacuum filter. The further purification of the decomposed liquor from the sulfuric decomposition is variable from manufacturer to manufacturer. This figure indicates treatment with granular carbon in fixed beds (25, 26), followed by demineralizing beds containing cation- and anion-exchange resins (27, 28). Double-or triple-effect evaporators (29) feed a separate crystallizer (30) and centrifuge (31). The mother liquor is recycled between feed to carbon cells (32) or to a liming tank (33). The damp citric acid crystals are remelted (35) and vacuum crystallized (36). This is followed by centrifuging (37), drying (39), size classification (40), and packaging (41). The degree of purity of the initial sugar source going into the fermentation can be a factor in determining the amount of purification necessary and the need for recrystallizing the final product. *(Miles Laboratories, Inc.)*

may be broken down into coordinated sequences of biochemical conversions with the aid of *A. niger* and various unit operations and chemical conversions. A selected strain of *A. niger* is grown from a test-tube slant through to a seed tank, or inoculum. This growth may take 36 to 48 h. For sequential steps see the description below Fig. 4.7.

Special strains of yeast, *Candida guillier mondii* and *Candida lipolytica*, have been developed to produce citric acid. *C. lipolytica*[34] produces it from paraffin in a continuous process.

[34]U.S. Patent 4,014,742.

LACTIC ACID

Lactic acid, 2-hydroxypropionic acid, is one of the oldest known organic acids. It is the primary acid constituent of sour milk, where it derives its name, being formed by the fermentation of milk sugar (lactose) by *Streptococcus lactis*. Commercially, lactic acid is manufactured by controlled fermentation of the hexose sugars from molasses, corn, or milk. Lactates are made by synthetic methods from acetaldehyde and lactonitrile, a by-product of Monsanto's[35] acrylonitrile operation. It has been only since 1930 that lactic acid has been produced commercially from the milk by-product whey. About 1×10^9 kg of dry whey is produced annually from cheese or casein production, and about half is wasted.[36] The technical grade is employed for deliming leather in tanning. Edible grades are used primarily as acidulants for a number of foods and beverages. The small amount of lactic acid remaining is converted into plastics, solvents, and certain other chemical products. The USP grade is an old, well-established standard pharmaceutical.

MISCELLANEOUS COMPOUNDS

MONOSODIUM GLUTAMATE. The amino acid glutamic acid may be prepared synthetically, but chemical preparation produces a racemic mixture. Since only the sodium salt of the naturally occurring L-glutamic acid is desired for food flavor enhancement, this necessitates an expensive resolution step. L-Glutamic acid can be obtained directly from fermentation of carbohydrates with *Micrococcus glutamicus* or *Brevibacterium divaricatum*. Many patents have been issued on variations of the process as this is one of the largest volume compounds produced by fermentation.[37]

L-LYSINE. L-Lysine may be formed by microorganisms acting on carbohydrates. The usual organisms are *Micrococcus glutamicus*, *Brevibacterium flavum*, *Corynebacterium acetoglutamicum*, and *Microbacterium ammoniaphilum*. Each of these organisms requires special conditions and/or special additives to produce the product in good yields.

DIHYDROXYACETONE. Dihydroxyacetone ($HOCH_2COCH_2OH$) is made by the action of sorbose bacterium fermentation of glycerin.[38] This is an ingredient of suntan lotion that creates an artificial tan. It is also valuable as a chemical intermediate and as a catalyst in butadiene-styrene polymerization. Fatty acid esters of the hydroxyl groups are excellent emulsifying agents.

PHARMACEUTICAL PRODUCTS. The pharmaceutical industry has long employed fermentation (biosynthesis) to manufacture some of its most important medicaments. See Chap. 40, where fermentation is presented for antibiotics, biologicals, vitamins, and hormones. Controlled microorganisms are a most important chemical processing agent and assist in performing very complicated chemical reactions, in many cases more economically than purely

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[35]Synthetic Lactic Acid, *Ind. Eng. Chem.* 51 (2) 55 (1964); *Chem. Eng.* 71 (2) 82 (1964).

[36]Fermentation Process Turns Whey into Valuable Protein, *Chem. Eng.* 82 (6) 36 (1975).

[37]Gutcho, *Chemicals by Fermentation*, Noyes, Park Ridge, N.J., 1973.

[38]U.S. Patent 2,948,658

chemical conversions. This is especially true for complicated structural changes to make derivatives of natural steroid hormones.

Detailed flowcharts (Fig. 6.5) are given for three antibiotics, penicillin, streptomycin, and erythromycin. Chemical synthesis is given in Chap. 6 for riboflavin, as well as fermentation processes.

ENZYMES

Tables 4.1 and 4.6 list certain enzymes, organic catalysts formed in the living cells of plants and animals, which are essential in bringing about specific biochemical reactions in living cells. Enzymes can be classified by their method of activity.[39]

Catalytic function	Name
Oxidation-reduction	Oxidoreductases
Group transfer	Tranferases
Hydrolysis	Hydrolases
Group removal	Lyases
Isomerization	Isomerases
Joining of molecules	Ligases

Over 3000 enzymes have been extracted and purified. An enzyme generally can be stored dry and cool for several months or even years, but in solution it may lose its catalytic ability in minutes or hours. Efforts to stabilize the catalytic ability of enzymes have resulted in their immobilization on a solid support which makes them more resistant to pH and temperature

[39]ECT, 3d ed., vol. 9, 1980, pp. 148–224.

Table 4.6 Typical Industrial Enzymes Sold Today

Enzyme	Application
Proteases	Cheesemaking
	Digestive aids
	Meat tenderizing
	Beer chillproofing
	Cereal syrups manufacture
	Leather manufacture
Carbohydrases	Starch hydrolysis
	Sucrose inversion
	Fruit juice and vinegar clarification
Nucleases	Flavor control
Hydrolytic enzymes	Destruction of toxic or undesirable components in food
Oxidases	Oxidation prevention and color control in food products
	Clinical diagnostics

SOURCE: *CHEMTECH*, 3 677 (1973); 4 47, 309, 434 (1974).

changes. When immobilized, an enzyme may remain active for months, even when suspended in water.

Several methods are available for immobilizing enzymes. The oldest is adsorption on an ion-exchange resin, but in use the enzyme is slowly leached into the solution. To eliminate loss during use the enzyme can be intermolecularly cross-linked with the support, covalently bonded to the surface of a chemically reactive support, or trapped in the interstices of a polymer by copolymerization with a suitable monomer.

The amylases are the most important of the carbohydrases. One of the newer applications is the use of glucose isomerase to change glucose to fructose. These enzymes are often made by submerged fermentation, starting with corn-steep liquor and cornstarch. This mixture, after proper sterilization and cooling, is inoculated with *Bacillus subtilis* and fermented. The amylase can be isolated by precipitation with isoamyl alcohol and centrifugation. More amylases are commercially produced than any other enzyme.

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Chapter 5

Pulp and Paper Industries

Cellulose is not only the most abundant organic substance available, it is a major component of woody plants and is constantly replaceable. Its conversion to paper products is the function of the pulp and paper industries which manufacture thousands of useful items from it. The national per capita production of pulp and paper was approximately 300 kg in 1981. The industry employs about 650,000 people and uses over 10,000 scientists and engineers. The manufacturing processes are complicated and difficult to control. The use of digital control devices has increased the efficiency of the industry and generally improved the economy of operation. Without good control devices, modern paper-making machinery could not function. Papermaking consumes many chemicals as shown in Table 5 .1. The pulp and paper industries are not only consumers of large quantities of chemicals but are the largest energy users in the country, for this is an energy-intensive business.

HISTORICAL.[1] Writing paper first appeared between 2500 and 2000 B.C., made from a tall reed called papyrus which grows along the Nile river in Egypt. Strips from the reed were glued together with starch. This sheet was superior to calf and goatskin parchments, clay bricks, waxed boards, and other writing materials available at that time. The Chinese invented good processes for paper manufactured from bamboo and cotton about A.D. 105 and continue to make good paper by hand today. Southern Europe learned of the process and began to manufacture rag paper near the end of the fourteenth century. English manufacturers became established in the seventeenth century, and a paper mill was established in the United States in 1690. At this time all European paper was made from cotton and linen rags. Book printing began with Gutenberg's bible and greatly increased the demand for paper.

About 1750 the beater was developed and adopted in Holland, hence it became the Hollander. In 1799, a Frenchman, Robert,[2] invented the process for forming sheet paper on a moving wire screen. During evolution and improvement, this became today's Fourdrinier machine. In 1809 the cylinder machine was invented by Dickinson and forced the Fourdrinier into the background, but by 1830 the Fourdrinier's superiority for making fine papers was established. In 1826, steam cylinders were first used for drying and the first Fourdrinier was received in the United States in 1827. Paper demand increased with lower prices and

[1]Hunter, *Papermaking, the History and Techniques of an Ancient Craft*, Dover, New York, 1974; Britt (ed.), *Handbook of Pulp and Paper Technology*, 2d ed., Van Nostrand Reinhold, New York, 1970.

[2]Clapperton, *The Paper-Making Machine. Its Invention, Evolution, and Development*, Pergamon, Oxford, 1967.

***Table* 5.1** Composition of a Metric Ton of Paper

The following ingredients are necessary to produce an average metric ton of paper, representative of a variety of grades.

Water	133,000 L	Power	4752 MJ
Sulfur	15.5 kg	Talc	28 kg
Magnesium hydroxide	20 kg	Synthetic fillers	10.5 kg
Lime	176.5 kg	Alum	14 kg
Salt cake (Na_2SO_4)	33 kg	Clay	66 kg
Caustic soda	29 kg	Rosin	6 kg
Chlorine	54 kg	Dye and pigments	8 kg
Starch	53 kg	Capital investments per metric ton	$704
Wood	4 m^3	Work hours per metric ton	12.4
Fuel 686 L of oil or 1 t of coal			

SOURCE: The Wisconsin Paper Council, see *Pap. Trade J.* 166 (16) 41 (1982)

advancing general education, so a rag scarcity developed. Keller of Saxony developed a mechanical process for making pulp from wood, but the quality of the paper produced was low. The soda process for making pulp from wood was developed by Watt and Burgess in 1851. In 1857, the American chemist, Tilghman was granted the basic patent (U.S. 70,485) for the sulfite process, which produced good, readily bleachable pulp. The kraft process (from the German word kraft = strong) resulted from basic experiments conducted by Dahl in 1884 in Danzig. This process is commonly also referred to as the sulfate process because sodium sulfate is used as a make-up chemical for the cooking liquor. The dissolving agent, however, is not Na_2SO_4. In 1909, the sulfate process was introduced into the United States. At that time, pulp production was divided into 48 percent mechanical, 40 percent sulfite, and 12 percent soda.

The sulfate process has come to dominate the industry (see Table 5.2), and in 1981 the distribution had become 10.5 percent mechanical and thermomechanical, 3.5 percent sulfite,

***Table* 5.2** U.S. Production of Wood Pulp (thousands of metric tons)

	1980		1981	
	Air-Dried Weight,	Distribution, %	Air-Dried Weight,	Distribution, %
Bleached sulfite	1,324	3.0	1,272	2.8
Unbleached sulfite	349	0.8	362	0.8
Bleached and semibleached sulfate/soda	17,237	38.6	18,198	39.6
Unbleached sulfate/soda	17,773	39.8	17,757	38.6
Semichemical	3,652	8.2	3,560	7.7
Groundwood and thermomechanical	4,324	9.7	4,826	10.5
Paper grade wood pulp, total	44,659	100	45,975	100
Dissolving and special alpha pulp for chemical conversion	1,327		1,201	
Total	1,368		1,239	

SOURCE: American Paper Institute.

78.2 percent sulfate, and 7.7 percent semichemical.[3] Pulp manufacture gradually developed into an industry of its own, serving other industries as well as paper manufacture. Rayon, cellulose esters and ethers, and cellulose nitrate for both plastic and explosive use have become commercially important and consume much high-quality wood pulp. The control and utilization of the industry's by-products have required much attention (Chap. 32). The creation of useful products from lignin and waste liquors represents increased income for the industry and a solution to the stream pollution problem, but the development has just really begun and most of the by-products are still regarded as wastes and burned.

USES AND ECONOMICS. In 1980 the production of paper and paperboard in the United States was about 59.7×10^6 t.[3a] The consumption of newsprint alone was estimated at 10.1×10^6 t and 61,000 t of wood pulp were produced. The United States consumes about half of the world's paper production.

MANUFACTURE OF PULP

Before paper can be made from wood, the cellulose fibers must be freed from the matrix of lignin which cements them together. The fibers may be separated by mechanical procedures or by solution of the lignin by various chemicals (Table 5.3). The pulp thus formed has its fibers recemented together to form paper when suitable additives are used. In 1981, 89.5 percent of the pulping was carried out by chemical means. Pulp made by mechanical or thermomechanical means is inferior in quality to that produced chemically; much of it goes into newsprint. The kraft process dominates the field with semimechanical means a poor second.

RAW MATERIALS. Cotton and linen rags, once the major sources of fibers for paper have now been largely supplanted by fibers from wood. About 20 percent of the pulp used in the United States is recycled, and Europe and Japan recycle an even larger percentage. Both hard (deciduous) and soft (coniferous) wood are used to make pulp, but softwood is preferred because the fibers are longer. Bark cannot be used because it is not fibrous and is difficult to bleach. Bark is removed at the pulp mill by one of two debarking methods. The first abrades off the bark utilizing friction between pulpwood logs tumbled about in a rotating, cylindrical drum. Stationary drums using cams to move the logs about utilize the same principle. The bark is carried away in a stream of water, strained out, and usually burned. One company in Oregon recovers wax and corklike material from bark. The more generally used method is hydraulic debarking. Here a jet of high-pressure water (at about 10 MPa) is directed tangentially to the log and strips away the bark cleanly, breaks it up, and sluices it away. Recovered bark is often compressed before burning to reduce the water content and facilitate combustion.

PULPING PROCESSES. All processes used for pulping have the same goal—to release the fibrous cellulose from its surrounding lignin while keeping the hemicelluloses and celluloses intact, thereby increasing the yield of useful fibers. The fibers thus obtained are naturally colored and must be bleached before they can be used for paper. Here again, the goal is to obtain good color without degradation and loss of yield.

There are many processes and variations of basic processes which can be used for making

[3] *Wood Pulp and Fiber Statistics*, American Paper Institute, 1981.

[3a] t = 1000 kg.

Table 5.3 Comparison of Three Types of Chemical Pulp

Type of Process	Kraft, or Sulfate, Pulp (Alkaline)	Sulfite Pulp (Acid)	NSSC
Cellulosic raw material	Almost any kind of wood, soft or hard	Coniferous; must be of good color and free of certain phenolic compounds	Hardwood chiefly used, some softwood *(small chip size, fiberized)*
Principal reaction in digester	Hydrolysis of lignins to alcohols and acids; some mercaptans formed	$RC{:}CR' + Ca(HSO_3)_2 \rightarrow (RCHCR'SO_3)_2Ca$	Lignin sulfonation and hemicellulose hydrolysis lead to formation of acetate and formate.
Composition of cooking liquor	12.5% solution of NaOH, Na_2S, and Na_2CO_3. Typical analysis of solids: 58.6% NaOH, 27.1% Na_2S, 14.3% Na_2CO_3. Dissolving action due to NaOH and Na_2S. Na_2CO_3 inactive and represents the equilibrium residue between lime and Na_2CO_3 in the formation of NaOH.	7% by weight SO_2, of which 4.5% is combined as sulfurous acid and 2.5% as calcium or $Mg(HSO_3)_2$. Cooking 1 t of pulp requires 175 to 220 kg of SO_2 and 55 to 68 kg of MgO. Recent significant trend toward use of $Mg(OH)_2$, NH_4OH as base to speed lignin solution	Na_2S buffered with Na_2CO_3 bicarbonate, or kraft green liquor. Concentration of 90–100 g/L of Na_2S. Cooking liquor does *not* complete freeing of fibers, but mechanical treatment does
Cooking conditions	Time 2–5 h; temp. 170–176°C; pressure 660–925 kPa	Time 6–12 h; temp. 125–160°C or higher; pressure 620–755 kPa	Time 48–36 min; corrugating-grade pulp from mixed hardwoods 12–15 min; temp. 160–180°C, pressure 660–1100 kPa

Chemical recovery	Most of process is devoted to the recovery of cooking chemicals, with incidental recovery of heat through burning organic matter dissolved in liquor from wood; chemical losses from system are replenished with salt cake, Na_2SO_4	SO_2 relief gas recovered; magnesium liquor recovered and reused after wood digestion and pulp washing	Characterized by high yield—65–85%. Pulping losses 35–15% of wood components. Special recovery methods and by-product utilization
Materials of construction	Digesters, pipelines, pumps, and tanks can be made of mild steel or, preferably, of stainless	Acid liquor requires digester lining of acid-proof brick; fittings of chrome-nickel steels (Type 316), lead, and bronze	Serious corrosion problems encountered in digesters and handling equipment; stainless-steel protection needed
Pulp characteristics	Brown color; difficult to bleach; strong fibers; resistant to mechanical refining	Dull white color; easily bleached; fibers weaker than kraft	Stiff, dense paper of low opacity; fibers approach chemical pulps in strength
Typical paper products	Strong brown bag and wrapping, multiwall bags, gumming paper, building paper, strong white paper from bleached kraft, paperboards such as used for cartons, containers, milk bottles, and corrugated board	White grades: book paper, bread wrap, fruit tissue, sanitary tissue	Unbleached: large percentage for corrugated board, also newsprint, specialty boards. Bleached: writing and bond papers, offset, mimeo, tissue, and toweling

pulp from wood. Some work better on softwood than hardwood, some give high-yield lower-quality papers, some give low-yield superior papers, etc. The major processes are: sulfate or kraft process, groundwood and thermomechanical process, semichemical process, and sulfite process. Considering the variety of wood available, the many uses of paper, and the complexity of the process, it is not surprising that Casey[4] differentiates 5 mechanical processes, 7 chemimechanical and thermomechanical processes, 5 semichemical processes, 3 high-yield chemical processes, 11 full chemical processes, and 2 processes suitable for dissolving (high or chemical) pulp. There are also a host of new processes (solvent, oxygen, catalytic, and enzymatic processing) that have been suggested. Most are technically possible but economically unfeasible. Bearing in mind that many variations are possible, an attempt is made here to describe typical solutions to the problems encountered in processing wood to pulp.

KRAFT PULPING. Kraft, or sulfate, pulping is an alkaline process by which most pulp is presently made. It is an outgrowth of the obsolete soda process which cooked with a strong (12%) solution of NaOH and Na_2CO_3. The soda process gave low yields and worked well only with short-fibered hardwoods. The material added to the cooking liquor for the kraft process is Na_2SO_4, hence the common name of the sulfate process. The cooking, however, is done with a solution containing Na_2S, NaOH, and Na_2CO_3 formed from the sulfate during preparation and recovery of the cooking liquor. Although all sorts of woods can be cooked by the kraft process and the fibers obtained are bleachable and strong, it is very important that the chemicals used can be recycled and regenerated, reducing or even eliminating stream pollution. Odoriferous materials released during cooking are, however, strong air polluters and difficult to control.

Most kraft processors use coniferous woods, and the process deals readily with the large amounts of oil and resins in these woods. Most processes built during the last 10 years employ continuous digesters, although some large batch units are still being built. Batch units offer good control, but continuous units require less investment for a given capacity and make pollution control installation simpler and smaller. The trend has been toward very large units.

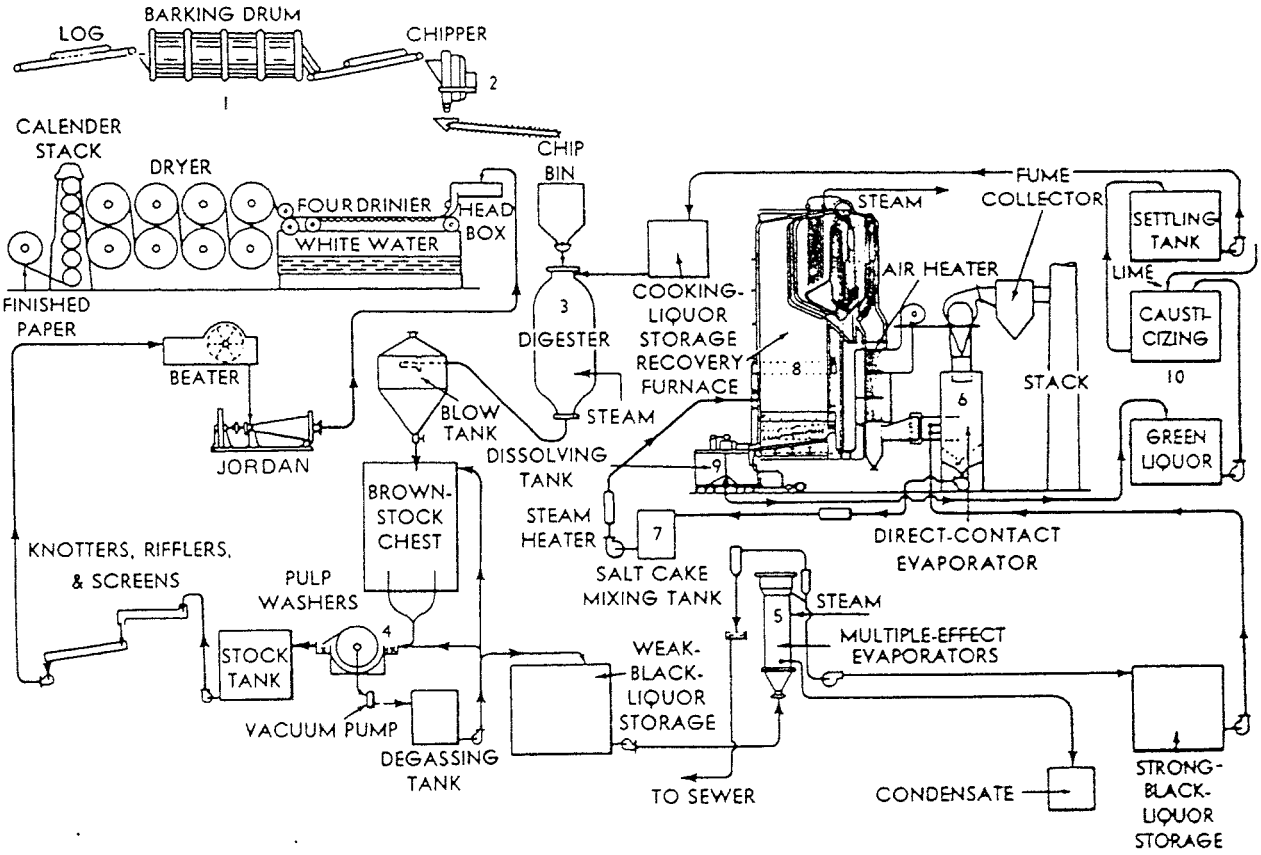
Figure 5.1 shows the overall kraft process including the important black liquor (processing chemical) recovery system. Table 5.3 summarizes the cooking conditions used for typical pulping procedures. Steam is usually recovered from the blow tank now, and the batch digester shown is generally replaced by a continuous one, the most popular unit being the Kamyr. A prehydrolysis step to remove pentosans and polyoses is common. The cooking process causes chemical reactions involving the hydrolysis and solubilization of the lignin, thus freeing the cellulose fibers. The turpentine is volatilized and sodium soaps are formed from the rosin acids. The hydrolysis frees mercaptans and organic sulfides which are the source of the foul odor associated with kraft mills.

When using a continuous digester, the manufacture of sulfate pulp involves the following sequences:

Logs are cut to convenient lengths and debarked as previously described, then conveyed to the chippers, which are large rotating disks holding four or more heavy knives. These reduce the wood to chips of preselected size

The chips are screened on either rotating or vibrating screens to separate the oversize chips, the desired product, and the sawdust. The oversize chips and slivers are sent to rechippers to reduce them to the proper size.

[4]Casey, *Pulp and Paper, Chemistry and Chemical Technology*, 3d ed., vol. 1, Wiley-Interscience, New York, 1980.



In order to produce 1 t of dried pulp, the following materials are required:

Wood	1.5–2 t	Steam	6500 kg
New lime	250 kg	Electricity	900 MJ
Soda ash	125 kg	Direct labor	5.5 work-h

Fig. 5.1. Flowchart for the kraft, or sulfate, pulping process with black-liquor recovery and reuse. Alkaline procedure. PROCESS NOTE: This flowchart is identical with one for the soda process, except sodium carbonate would be added instead of sodium sulfate (salt cake) *(Babcock and Wilcox Co.)*.

Chips enter the continuous digester and are presteamed at approximately 100 kPa, volatilizing the turpentine and noncondensable gases. They then pass to a higher-pressure impregnation zone at about 900 kPa, where their temperature is adjusted and they meet with the cooking liquor. Cooking time is about 1½ hours at 170°C. A quench flow of cold cooking liquor quickly stops the cooking reaction. Countercurrent displacement washing then reduces the chemical content of the chips, and the pressure is then reduced, producing flash steam which is used for the presteaming step on the entering chips.

The chips thus produced, along with their adhering liquor, are known as brown stock. Some method of heat recovery from this material usually precedes the washing step.

Pulp washing is an operation being aggressively studied now in hopes of reducing water use and simplifying water reclamation processes. High-density displacement washing is displacing the old repulping and straining procedures.

The spent cooking liquor, commonly called black liquor, is now ready to be treated to recover its chemical content for reuse and its organic content as heat. The black liquor recovery process is in many ways more difficult to run economically than the pulping process itself.

The washed pulp is passed over screens to remove knots, unreacted chips, slivers, trash, etc., then sent on to thickeners and filters.

The thickened pulp is next bleached, and here again, the technique is in a state of flux.[5] Chlorine and hypochlorite, the original materials used to oxidize and destroy the dyes and tannins of the wood, leave chloride residues in the wash water and harm the cellulose fibers. Chlorine dioxide is less damaging than Cl_2 or hypochlorite and is generally used in the first stage of a multiple-stage bleaching process. Bleaching is often done in dilute solutions followed by pulp concentration by dewatering and may use much water, contaminating all of it. Bleaching at high pulp consistencies is possible and highly desirable. Bleaching by reducing agents usually employs sodium dithionate $Na_2S_2O_4$, sodium borohydride, or bisulfite. Oxidative bleaches are ozone, Na_2O_2, H_2O_2, ClO_2, and chlorine.

After bleaching, the pulp is washed and rethickened in preparation for making it into coarse sheets dry enough to fold into a bundle, store, and ship—these are called laps. The pulp may also be used directly for making paper.

Laps are made on a wet thickener consisting of a suction cylinder dipping into a vat filled with fiber suspension. The cylinder discharges its load onto an endless felt belt which carries the pulp through squeeze rolls, then a series of press rolls. The resulting laps contain 35 to 45% air-dry fiber. The moisture is reduced further by stacking the laps in a hydraulic press and pressing them at around 20 MPa. The laps emerge with 50 to 60% air-dry fiber.

Kraft pulp, made from coniferous woods, has the longest fibers of all the pulps. This, coupled with the fact that the chemicals used are not so harsh in their action as those employed for other chemical pulps, makes possible the production of very strong papers. In the past, the dark color of kraft paper limited its use mainly to wrapping papers, sacks, and paperboard. Newer developments in the bleaching treatment have made possible the manufacture of light-colored and white pulps, allowing the mixing of this very high-strength pulp with other types to increase the paper strength.

Recovery of the Black Liquor.[6] An essential factor in the kraft process has been the recovery of the spent liquor from the cooking process. The black liquor removed from the pulp in the pulp washer, or diffuser, contains 95 to 98% of the total chemicals charged to the digester. Organic sulfur compounds are present in combination with sodium sulfide. Sodium carbonate is present, as are also small amounts of sodium sulfate, salt, silica, and traces of lime, iron oxide, alumina, and potash. Total solids usually average about 20%. This black liquor is concentrated, burned, and limed as shown in Fig. 5.1. In the smelting furnace any remaining organic compounds are broken down, the carbon burned away, and the inorganic chemicals melted. At the same time, the reaction

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$

takes place. The carbon (reducing agent) comes from the organics in the wood.

The Thomlinson kraft recovery furnace is the unit presently most widely used for burning concentrated black liquor. Black liquor is concentrated to around 35% solids in multiple-effect evaporators, then the solution is sprayed directly into the Thomlinson furnace; there it is burned, the reduction of the sulfate to sulfide takes place, steam is made, and a molten salt mixture, or smelt, is produced. These complicated, often conflicting chores make adjustment and control of the furnace very difficult. A hazard exists because the molten smelt can cause

[5]Kohn, Pulp-Bleaching Process Cuts Costs, Time, Effluent, *Chem. Eng.* 54 (5) 136 (1977).

[6]Chase (ed.), *The Use and Processing of Renewable Resources*, AIChE Symposium Series 207, vol. 77, 1981.

explosions if it comes in contact with small amounts of water. Hydropyrolysis of dry black-liquor solids to produce combustible gases has been suggested, and fluidized-bed combustion of a 35% solution to produce chemical pellets instead of smelt has been tried. All the alternatives to the present system have some disadvantages and/or difficulties, but it seems probable that a more energy-efficient recovery system than the present one will shortly be forthcoming.

The molten chemical *smelt* is allowed to fall into a weak solution in tank 9 of the "dissolving liquor" coming from the causticizing plant. The chemicals dissolve immediately to give a characteristic green liquor. The insoluble impurities are allowed to settle out, and any carbonate is then causticized by adding slaked lime prepared from recovered calcium carbonate. The reaction

$$Na_2CO_3(aq) + Ca(OH)_2(s) \rightarrow 2NaOH(aq) + CaCO_3(s) \qquad \Delta H = -8.79 \text{ kJ}$$

occurs quickly. The resulting slurry is separated in settlers and rotary continuous filters, using Monel metal screens as a filtering medium. The calcium carbonate sludge, or "mud," is sent to a lime kiln to recover the calcium oxide for reuse in the process. The filtrate is the white liquor used in the cooking of the fibers. It contains sodium hydroxide, sodium sulfide, and small quantities of sodium carbonate, sodium sulfate, sodium sulfite, and thiosulfate.

Among the by-products from the black-liquor recovery plant is tall oil (Chap. 32), a black, sticky, viscous liquid composed mainly of resin and fatty acids. The tall oil may be separated from the weak black liquor by means of centrifuges (in America) or obtained by flotation from the concentrated liquors (in Europe). The digester relief gases yield paying quantities of turpentine, from 11 to 42 L per metric ton of pulp produced. This may be refined to produce sulfate turpentine.

SODA PULPING. Soda pulping is brought about by a procedure similar to that used for sulfate pulp, except that the dissolving agent is $NaOH/Na_2CO_3$ and the make-up chemical is Na_2CO_3 instead of Na_2SO_4. Its importance is too small to warrant additional details here.

SULFITE PULPING

Sulfite Pulp. The quantity of pulp made by this process steadily diminishes despite its high quality, because of the water pollution problems which it causes. Although spruce is the wood most commonly employed, appreciable quantities of hemlock and balsam are also used. The wood is barked, cleaned, and chipped as described for sulfate pulp, the resulting chips being about 1.5 cm in length. It is then conveyed to storage bins above the digesters preparatory to being cooked. The chemistry of the sulfite digestion of cellulosic materials is no more well understood than that of the sulfate process. Energy requirements are high. The usual sulfite process consists of digestion of the wood in an aqueous solution containing calcium bisulfite and an excess of sulfur dioxide. The sulfite process involves two principal types of reactions, which are probably concurrent: (1) sulfonation and solubilizing of lignin with the bisulfite, and (2) hydrolytic splitting of the cellulose-lignin complex. The hemicelluloses are also hydrolyzed to simpler compounds and the extraneous wood components acted on. Since disposal of waste liquor (more than half of the raw material entering the process appears here as dissolved organic solids) creates a serious water pollution problem, concerted attention has been turned to its removal or utilization. A slurry of magnesium oxide is substituted for lime,[7]

[7]Hull et al., Magnesia-Base Sulfite Pulping, *Ind. Eng. Chem.* 43 2424 (1951) (excellent article, flowcharts, pictures).

because then chemical and heat recovery are possible, and a solution to the disposal problem of the waste liquor is also provided. Sodium and ammonia[8] have also been substituted for calcium as a pulping base in a limited way. The waste liquor from the calcium sulfite process cannot have its values used over again, since the calcium sulfite does not decompose to sulfur dioxide, whereas magnesium sulfite does. $CaSO_4$ is formed and lost. Hence the newer and technically more acceptable[9] sulfite process is based on magnesium bisulfite rather than the earlier used, corresponding calcium compound, resulting in a greater concentration and more active combined sulfur dioxide, without danger of precipitation and with a quicker separation and solution of the noncellulose wood constituents (lignin and hemicelluloses) (Fig. 5.2).

The essential reactions involved in the preparation of the cooking liquor are quite simple:

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + H_2O + CaCO_3 \rightarrow Ca(HSO_3)_2 + CO_2$$

or

$$2SO_2 + H_2O + MgCO_3 \rightarrow Mg(HSO_3)_2 + CO_2$$

$$2SO_2 + Mg(OH)_2 \rightarrow Mg(HSO_3)_2$$

or

$$SO_2 + H_2O + NH_3 \rightarrow NH_4HSO_3$$

The entire process may be divided into the following sequences, as illustrated in Fig. 5.2 for the magnesium bisulfite process.

Sulfur is melted in a tank heated by the rotary burner and then fed to this burner for oxidation.

Any sulfur that is vaporized in the burner enters a combustion chamber, where it is oxidized to sulfur dioxide. The amount of air in this operation is closely controlled to prevent the formation of sulfur trioxide.

The sulfur dioxide obtained is cooled quickly in a horizontal, vertical, or pond cooler consisting of a system of pipes surrounded by water.

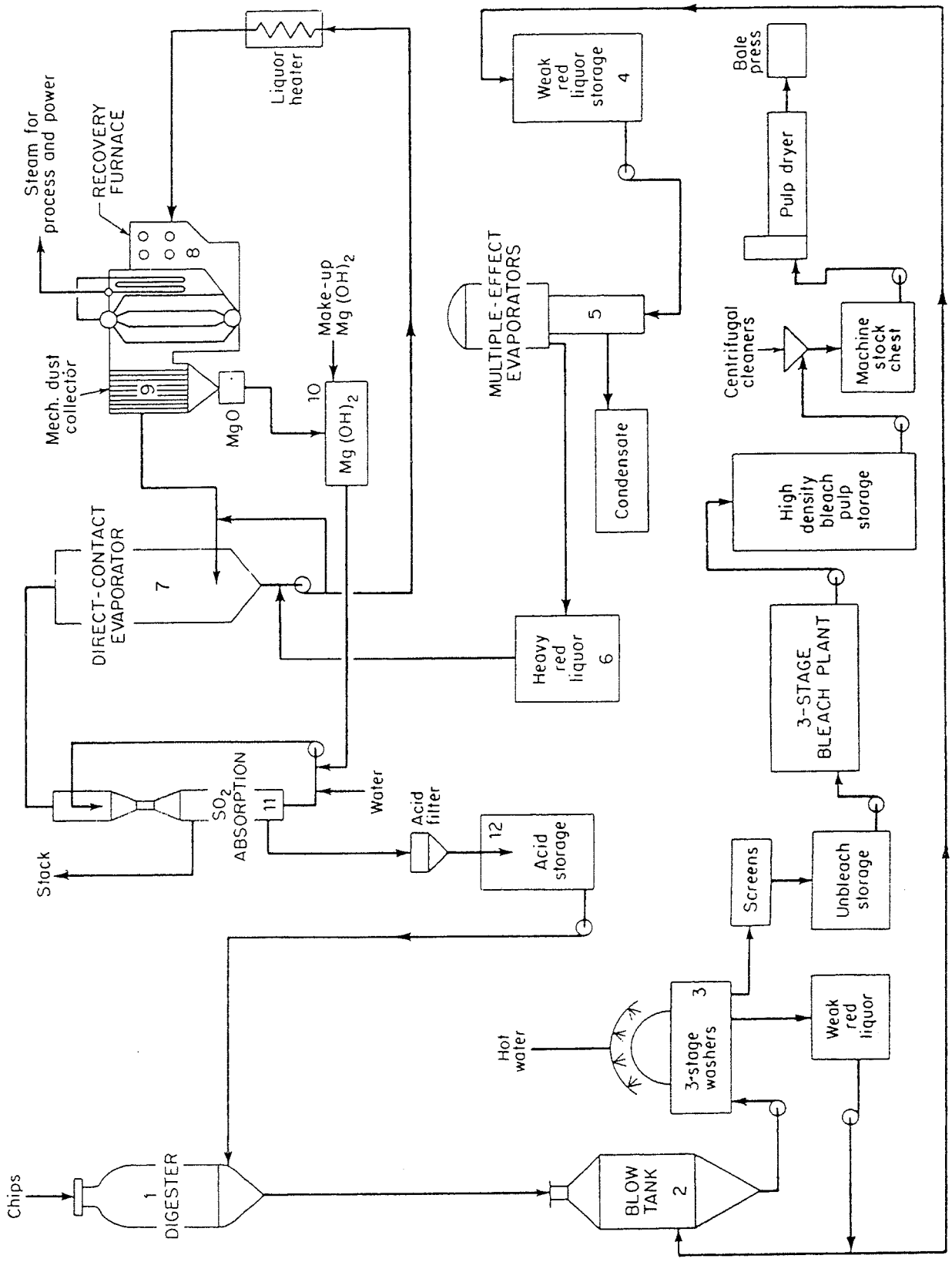
The absorption of the gas in water, in the presence of calcium, magnesium, or ammonium compounds, is accomplished in a series of two or more absorption towers or acid-making tanks

[8]Ammonia Base Sulfite Pulping at Inland Container, *Pap. Trade J.* November 20, 1972.

[9]Liquor-Making Eased for Mg-Base Pulp Mills, *Chem. Eng.* 71 (15), 80 (1964); It's a Big Job to Clean up Sulfite Waste, *Chem. Week.* 110 (17) 37 (1972); New Cleanup Methods Vie for Sulfite Pulping Jobs, *Chem. Week* 111 (17) 67 (1972).

PULP GRADES	DISSOLVING	NEWSPRINT
Yield of pulp, %	35	60
Materials Consumed per Metric Ton, kg		
Wood, oven dried	2572	1500
Magnesium oxide	61	75
Sulfur dioxide	195	240
Steam	1450	1000
Power, MJ	14,526	10,026

Fig. 5.2. Flowchart of Magnefite pulping and magnesium oxide recovery. Improved acid sulfite pulping. *(Babcock and Wilcox Co.)*


Chips
1
DIGESTER
BLOW TANK
2
3-stage washers
3
Hot water
Weak red liquor
Screens
Unbleach storage
3-STAGE BLEACH PLANT
High density bleach pulp storage
Centrifugal cleaners
Machine stock chest
Pulp dryer
Bale press
Weak red liquor storage
4
MULTIPLE-EFFECT EVAPORATORS
5
Condensate
Heavy red liquor
6
DIRECT-CONTACT EVAPORATOR
7
Steam for process and power
RECOVERY FURNACE
8
Liquor heater
Mech. dust collector
9
MgO
10
Mg (OH)2
Make-up Mg (OH)2
SO2 ABSORPTION
11
Water
Acid filter
12
Acid storage
Stack

for $Mg(HSO_3)_2$. A fine spray of the suspension passes down through the tower system countercurrent to the sulfur dioxide gas, which is blown up through the tower.

The liquor contains a certain amount of free sulfur dioxide, which is enhanced from time to time as the free sulfur dioxide vented from the digesters is bubbled through acid-making towers. The final liquor, as charged to the digesters, is a solution of calcium, magnesium, or ammonium bisulfites, analyzing about 4.5% "total" sulfur dioxide and about 3.5% "free"[10] sulfur dioxide. The digester is filled with chips, and the acid cooking liquor is pumped in at the bottom. The digesters are cylindrical steel vessels with a capacity of from 1 to 20 t of fiber and 10,000 to 200,000 L of "acid." A special acid-resisting lining is used to avoid the corrosive action of the cooking liquor.

The digester is heated with direct steam. In recent years the industry has turned to digesters with forced outside circulation, which heat the cooking liquor in an outside stainless-steel tube heater and circulate it through the charge by means of pumps. This permits better temperature distribution through the charge and prevents dilution of the liquor with the direct steam injection formerly used for heating. Conditions of the cook depend on the nature of the wood, the composition of the acid, and the quality of pulp charged. The pressure varies from 480 to 1100 kPa, depending upon the construction of the plant. The time and the temperature range from 6 to 12 h and from 170 to 176°C.

At the end of the cooking process the digester (1) is blown to a tank (2) a large, round tank having a false bottom and equipped with means to wash the pulp with fresh water. The cooking, or weak red liquor is evaporated (5–7) and burnt in a boiler (to provide steam) (8,9). MgO and sulfur dioxide are formed. The MgO is slaked (10) and pumped to the cooling and acid tower (11) down which the sulfur dioxide (regained and make-up) is passed to make fresh bisulfite liquor (12).

The pulp is pumped from the blow tank (2) to a series of screens (3), where knots and large lumps of fiber are removed. The accepted stock from the screens is sent to rifflers, or centrifuges, to remove foreign matter.

The relatively pure pulp is concentrated in thickeners, which are cylindrical frames covered with 80-mesh wire. The water passes through, and the pulp is retained on the screen.

The pulp is sent to the bleacher, where chlorine dioxide is introduced. After the chlorine has been exhausted, milk of lime is added to neutralize the mass.

The stock is washed, thickened and sent to the machine stock chest.

Pulp from the chest is formed into laps of about 35% dry-fiber content, and the laps are dried with steam-heated rolls in a pulp dryer and baled as a product which is 80 to 90% dry fiber.

The system of preparing the cooking liquor consists of slaking burnt lime containing a high percentage of magnesia with warm water to produce a 1°Bé suspension. This solution is treated with sulfur dioxide gas to produce the cooking liquor.

Sulfite pulp is a high-grade type of pulp and serves in the manufacture of some of the finest papers, including bond. It is used either alone or with some rag pulp to make writing paper and high-grade book paper. It furnishes dissolving pulps for plastics, synthetic fibers, and other products in which wood per se is unrecognizable.

It is easy to bleach, but the fibers are weak and the process began to be replaced as soon as the ClO_2 bleaching process made kraft bleaching practical.

[10]In the parlance of the pulp manufacturer, the "free" sulfur dioxide is the sum of the sulfurous acid and that portion which requires alkali to convert from a bisulfite to a neutral sulfite.

Waste Sulfite Liquor. Calcium-based sulfite waste liquor does not permit recovery and reuse of either the Ca or S content. Magnesium- and ammonium-based liquor can be recovered simply, but the ammonia cannot be recovered. Sodium base can be recovered, but the recovery process is complex. Only the magnesium base is conveniently and simply handled, and this explains the reason why it is preferred. Until recently, it was common practice to use calcium base and simply dump the waste liquor into a nearby stream. A combination of public attention to water pollution and the necessity for recovering expensive chemicals has stopped this. Figure 5.2 shows the method for recovery and reuse of magnesia-based waste liquor. The dissolved organic matter is used to provide heat for the process.

Strong efforts to make better use of sulfite waste liquor than burning it have been made. Processes for recovering lignin; making vanillin from the lignin; and making tanning materials, road binders, portland cement accelerators, core binders, and food yeast have been developed.

SEMICHEMICAL, OR NSSC, PULPING. Neutral sulfite semi-chemical (NSSC) pulping uses substantially less chemicals in pulping than the full chemical processes. The yield of pulp obtained from a given wood is, however, much higher. Most such pulps are used in linerboard and corrugating paper. Yields of pulp are as high as 65 to 80 percent, which makes for better use of the wood. Quality and bleachability are, of course, somewhat poorer. Continuous and batch digestors are both used. The idea is to make a mild cook weaken the binding material between the fibers, then separate them by mechanical means. Sodium sulfite buffered with sodium carbonate is the usual cooking medium, but other pulping agents, such as kraft green liquor can also be used, along with elevated temperatures to give enough softening to permit mechanical refining. The high yields obtained reduce stream pollution problems.

MECHANICAL AND THERMOMECHANICAL PULPING. Stone-ground wood involves no chemical treatment. Soft coniferous species such as spruce and balsam are the chief woods employed. Debarked logs are held at an acute angle against a rotating stone so that the fibers will be torn apart rather than broken. Water is provided to remove the heat of friction and to carry the dislodged fibers away. "Pockets" around the face of the grindstone hold logs against it under pressure from hydraulic cylinders. The freed fibers are dropped into a container known as the stock sewer and passed along to a sliver screen. Here the fine material passes through into the stock pit and the coarser particles are separated and sent to some type of refiner, then returned to the screens. The fines are concentrated in thickeners, yielding mechanical pulp. The water overflow from the thickeners contains 15 to 20 percent of the original fiber and is recirculated to the grinders and used to facilitate flow in the stock sewers. As the process continues to operate, it is necessary to add fresh water to the system to keep the temperature down, so some white water must be removed. After straining out its valuable fibers, it is sent to waste. The only chemical change occurring during the process is a slight hydration of the cellulose due to its long contact with warm water.

Groundwood is used chiefly for cheaper grades of paper and board where permanency is not required. Chemical decomposition of the noncellulosic constituents sets in and results in eventual brittleness and discoloration. Mechanical pulp is rarely used alone. Even in the manufacture of newsprint, cheap Manila, wall, tissue, and wrapping papers, the mechanical pulp is usually mixed with a small amount of chemical pulp to add strength and improve color.

Groundwood pulp can be bleached, although not to the brightness of chemical pulp. Sodium and calcium bisulfites were the first bleaches used, but oxygen, ozone, chlorine dioxide, and sodium and hydrogen peroxide have proved to be more effective. Bleaching is an

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expensive process, as is any process consuming chemicals, and must be carefully designed to give the maximum brightness and fiber strength with a minimum of cost and degradation.

Thermomechanical pulping takes advantage of the fact that elevated temperatures soften the lignin and make mechanical pulping less difficult. The wood is steamed at around 975 kPa, and the refining is carried out at the high temperature (170°C) thus obtained. The fiber obtained is coated with lignin and highly suitable for fiberboard, but makes poor paper.

NEW PULPING PROCESSES. Solvent pulping[11] with a variety of solvents such as ethanol, phenol, and other delignifying solvents that contain no sulfur continue to be suggested. The holopulping process developed by the Institute of Paper Chemistry uses chlorine dioxide as a pulping agent. Straight oxygen and nitric acid pulping have also been suggested. One of the more interesting ideas involves using anthraquinone in small quantity as a catalyst in ordinary pulping processes to speed them up. A few of these processes have reached the pilot plant stage, but paper companies show little inclination to gamble on risky new projects even when there are apparent savings in energy and the possibility of salable new by-products.

SECONDARY FIBER PULPING.[12] Over 20 percent of U.S. paper now comes from the repulping of recycled paper. There are a great many grades produced varying widely in quality. Batch processes are usually used. The collected material is repulped in water, cleansed of objectional dirt and contaminants, deinked with alkali [NaOH, Na_2CO_3, and $Na_2O(SiO_2)_x$], washed, cooked lightly with mild alkali, bleached, screened, then handled like any other pulp. Secondary fiber is worth about 5 times its value as waste paper. The largest single use is in the manufacture of multi-ply cylinder board. Here several sheets formed on a cylinder machine are combined to give a heavy paper. The outside layers may be virgin stock with the inside layers secondary fiber. Six major grades are generally recognized: chipboard, mill board, folding boxboard, combination Manila board, container board, and setup board. A continuous cooking process is also being used.

RAG PULPING. The oldest material used for making paper, and the material still used for the finest grades, is cotton in the form of rags or cotton linters (the cotton fuzz adhering to cotton seeds after ginning). Old rags make pulp suitable only for felts, so clippings from textile manufacturing plants and clothing manufacturers are the major sources of raw material. Mixed fibers containing synthetics are undesirable, but rayon is quite suitable. Dyes can be removed with strong reducing agents. Rags must be chopped and cooked to remove sizing materials and then are treated in small batches in horizontal rotary cookers for 2 to 10 h at around 300 kPa. The rags are usually chipped into the short lengths needed for paper making before cooking. This business is quite small, and the equipment has not been much modernized. Paper made from rags has a much longer storage life than that made from wood fiber.

DISSOLVING PULP. Where pulp is to be used for making cellulose derivatives, it is important that it be essentially pure α-cellulose.[13] Cotton linters are almost pure α-cellulose, but the

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[11]Katzen, Frederickson, and Brush, The Alcohol Pulping and Recovery Process, *Chem. Eng. Prog.* **76** (2) 62 (1980); Schweers, Phenol Pulping—A Potential Sulfur-Free Papermaking Process, *CHEMTECH* **4** (8) 490 (1974).

[12]Secondary Fiber Technology, *Tappi* **58** (4) 78 (1975); Paper Recyclers Regroup, *Chem. Eng.* **81** (12) 44 (1974).

[13]α-Cellulose is the technical term used in the trade. α-Cellulose is insoluble in an 18% NaOH solution after it is diluted. The standards for the test are available in ASTM publications.

supply is not sufficient to meet the demand. Dissolving pulp is made by posttreatment of high-quality sulfite pulp with sodium hydroxide or from pre-hydrolyzed sulfate pulp. Such purified cellulose commands a premium price.

MANUFACTURE OF PAPER

WET PROCESS. The various pulps, even though frequently manufactured in coarse sheets, still lack those properties which are so desirable in a finished paper, such as proper surface, opacity, strength, and feel Pulp stock is prepared for formation into paper by two general processes, beating and refining. There is no sharp distinction between these two operations. Mills use either one or the other alone or both together. However, the beater is of decreasing importance with the increasing use of continuous refining. The operation of refining fits in well with the trend toward automatic mills.

The most generally used type of *beater* (also known as a Hollander, Fig. 5.3) consists of a wooden or metal tank having rounded ends and a partition part way down the middle, thus providing a channel around which the pulp circulates continuously. On one side is a roll equipped with knives or bars, and directly below this is a bedplate consisting of stationary bars. In operation, the circulating pulp is forced between the bars on the revolving roll and the stationary bars of the bedplate. The roll itself may be raised or lowered to achieve the results desired. Beating the fibers makes the paper stronger, more uniform, more dense, more opaque, and less porous. Bonding between fibers is increased by beating.

Most mills use some variation of the conical refiner, or Jordan engine (Figs. 5.4 and 5.5). Stationary bars of metal or stone are set inside the conical housing. The rotor is fitted with metal bars set to close clearance against the shell. Pulp enters the small end of the cone and passes out the other. The pulp is deformed, defibered, and dispersed, but not cut by the device.

Disk refiners perform similar duties by passing the pulp between rotating grooved disks.

In addition to fiber, paper also contains fillers, sizes, and frequently, dyes. These materials are generally added during the refining process. Various types of pulps are blended to give the desired properties, then the filler and color are added to the mixture and beaten to uniformity. Alum is then added to coat the fibers and coagulate the materials present. All papers except the absorbent ones (tissue, toweling, filter) require a filler to give a smoother surface, a more brilliant whiteness, improved smoothness and printability, and improved opacity. Fillers are always finely ground inorganic materials, usually naturally occurring substances such as talc or special clays or manufactured materials such as titanium dioxide, precipitated calcium carbonate, or certain silico-aluminates. The quantity of paper produced, by grades, is shown in Table 33.4.

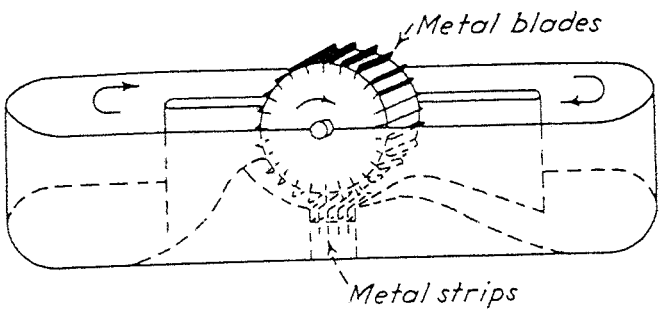

Fig. 5.3. Beater or Hollander.

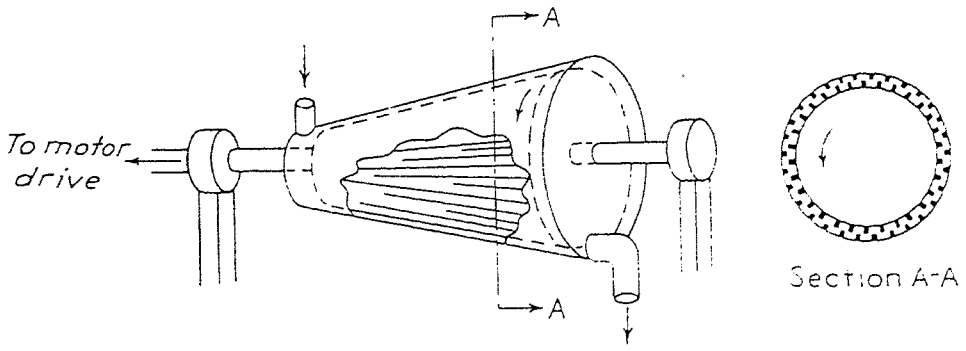

Fig. 5.4. Conical refiner or Jordan engine.

Sizing[14] is added to paper to improve resistance to penetration by liquids. Sizing may be added to the furnish (mixed pulp diluted and ready to add to the paper machine) or applied to the surface of the finished paper. Stock sizing involves adding size in the beater, then later precipitating it with papermaker's alum, $Al_2SO_4 \cdot 18H_2O$. The commonest sizing agent is rosin soap made from tall oil; wax emulsions are also used. Stock sizing forms a gelatinous film on the fiber which loses its water of hydration to produce a hardened surface. Tub sizing uses suitable solutions which, applied to the dried paper and calendered (ironed), produce a firm nonporous surface. Common tub sizes are modified starches and plastic materials. Such sizing is usually done on the dry end of the paper machine itself, but separate size presses are also used. The ability to take ink well, ink properly, resist moisture, and withstand erasure is all greatly improved by this process.

Conventional papers have wet strengths of less than 10 percent of their dry strength. Amino-aldehyde synthetic resins have been found to impart wet strength without causing water repellancy, and this has resulted in important additional uses for paper.[15]

Two types of conventional wet process paper machines are in use, the Fourdrinier machine

[14]Davison, The Sizing of Paper, *Tappi* 58 (3) 48 (1975) (a review)

[15]Thode et al., Mechanism of Retention of Wet Strength Resins, *Tappi* 42 (3) 178 (1959); 43 (10) 861 (1960); 44 (4) 290 (1961).

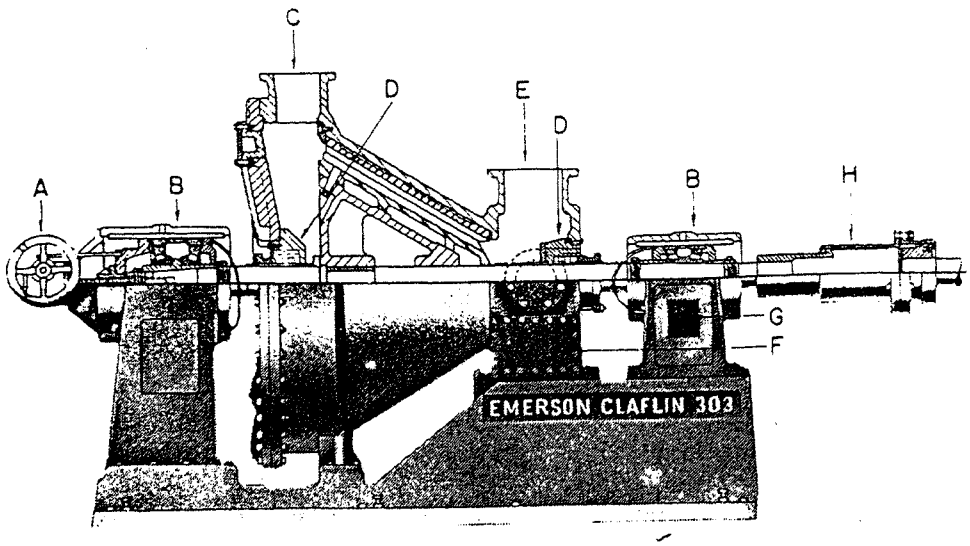

Fig. 5.5. Emerson Claflin refiner. (A) Plug adjustment mechanism, (B) bearing assemblies, (C) stock outlet, (D) packing boxes, (E) stock inlet, (F) cleanout, (G) oil-mist lubrication, (H) coupling, coupling. *(Emerson Mfg. Co.)*

***Table* 5.4** Paper and Paperboard Products, by Grades (in millions of metric tons)

	1975	1979	1980
Paper and paperboard, all grades	51.2	65.0	63.5
Paper	25.7	34.3	34.3
Newsprint	8.5	10.2	10.7
Coated printing and converting	2.8	4.2	4.3
Uncoated book and other printing	7.0	10.4	10.3
Packaging and industrial converting	3.9	5.4	5.1
Tissue and other machine-creped	3.5	4.1	3.9
Paperboard	21.2	26.4	24.9
Unbleached kraft	9.5	12.3	11.7
Bleached fiber	2.8	3.1	2.7
Semichemical	3.3	4.3	4.3
Recycled furnish	5.6	6.7	6.2
Construction paper and board	4.3	4.3	4.3

SOURCE: *Statistical Abstract of the United States*, 1981.

and the cylinder machine. Both form the paper by draining water from a dilute fiber mix through a fine screen and both dry the mat thus formed by dewatering with rollers, drying on heated rolls, and smoothing with calenders.

FOURDRINIER MACHINE. Figure 5.6 shows the essential parts of a Fourdrinier machine. The very dilute stock from the foregoing operations, containing approximately ½% fiber, is first sent through screens to the head box from which it flows through a calibrated sluice onto a moving, endless wire screen. The pulp fibers remain on the screen, while a great portion of the water drains through. As the screen moves along, it has a sidewise shaking motion which serves to orient some of the fibers and to give better felting action and more strength to the sheet. While still on the screen, the paper passes over suction boxes to remove water and under a dandy roll which smooths the top sheet. Rubber deckle straps along the sides of the screen serve to form the edges of the paper.

From the wire, the paper is transferred to the first felt blanket, which carries it through a series of press rolls, where more water is removed and the paper given a watermark if so desired. Leaving the first felt, the paper passes through steel smoothing rolls and is picked up by the second felt, which carries it through a series of drying rolls heated internally by steam. The paper enters the rolls with a moisture content of 60 to 70% and leaves them 90 to 94%

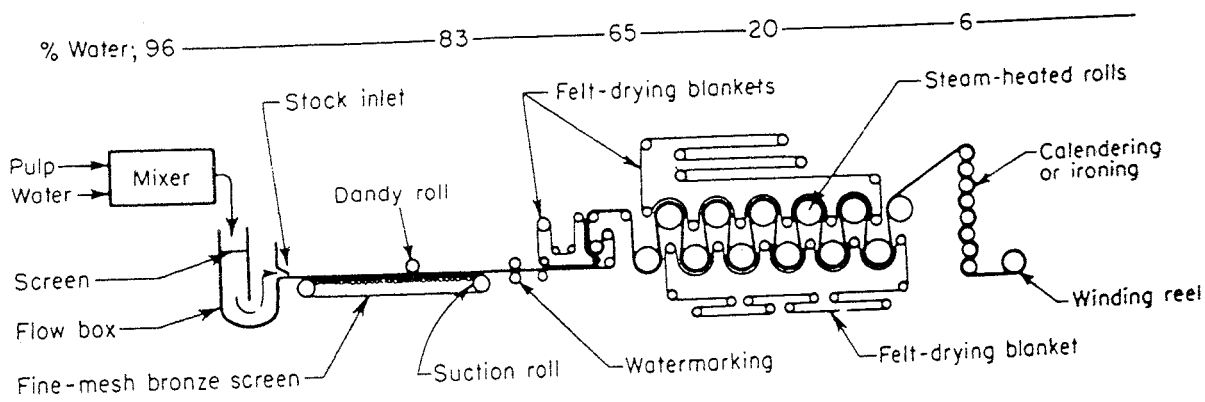

Fig. 5.6. Fourdrinier machine.

dry. Sizing may be applied on the sheet at this point, in which case it must pass through another series of drying rolls before entering the calender stack, which is a series of smooth, heavy, steel rolls which impart the final surface to the paper. The resulting product, finished paper, is wound on the reel. The enormous quantity of water used makes it necessary to recirculate as much of it as possible for economical operation. The operation of a Fourdrinier is a complex procedure. One of the major problems is making suitable allowance in the speed of the various rolls for the shrinkage of the paper as it dries. The operating speeds of the machine vary from 60 to 1800 m/s. The control of the temperatures, speeds, and consistencies of the parts of the paper machine is very complex, and had always been viewed as an art until computer control became available. Now computer control makes possible far less production of nonspecification paper; far fewer web breaks, which produce paper that must be rerun (broke); and faster and easier changing of one grade of paper to another. Computer control has been most satisfactory.

Cylinder machines are employed for the manufacture of heavy paper, cardboard, and nonuniform paper. The cylinder machine has from four to seven parallel vats, into each of which dilute paper stocks are charged. This allows several similar or dissimilar layers to be united in one heavy sheet. A wire-covered rotating cylinder dips into each vat. The paper stock is deposited on the turning screen as the water inside the cylinder is removed. As the cylinder continues to revolve, the paper stock reaches the top, where the wet layer comes in contact with and adheres to a moving felt. The traveling felt, carrying the wet sheet underneath, passes under a couch roll where some of the water is pressed out. This felt and paper come in contact with the top of the next cylinder and pick up another layer of wet paper. Thus a composite wet sheet or board is built up and passed through press rolls and on to the drying and smoothing rolls. Such a composite may have outside layers of good stock, whereas the inside ones may be of groundwood pulp.

A new process[16] combining the pressing and drying stages of the Fourdrinier, using hardwood pulp, and drying while under pressure has been disclosed. The process has been piloted at the U.S. Forest Products Laboratory in Madison, Wisc., and a commercial plant design is underway.

DRY PROCESSES. Considerable interest in a dry process[17] for making paper and nonwoven fabrics exists because of the cost and complexity of drying equipment and the enormous process-water demands of conventional methods. Pilot plants have been built to make paper by dry processes, but there are difficult problems as yet unresolved.

COATED PAPERS. Specialty papers are often coated with wax or plastic materials to impart special properties such as printability or resistance to fluids. Functional coatings are especially important for food products. The principal types of processes and equipment required for coatings are discussed in the Technical Association of the Pulp and Paper Industry Monographs.[18]

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[16]A Cheaper Process for Making Better Paper, *Chem. Week* 129 (13) 24 (1981).

[17]Danish Firm Tests Dry Process for Paper, *Chem. Eng. News* 45 (6) 40 (1967); Sorenson, Analyzing the Use of High-Bulk Filters on Air Formed Paper/Non-woven Output, *Pap. Trade J.* **166** (11) 26 (1982).

[18]TAPPI Monograph Series (current literature available from TAPPI).

SPECIALTY PAPERS. There are hundreds of uses for paper and as many hundreds of types produced, all classified according to their broad use (Table 5.4). Special industrial papers are those not falling into the specific broader-use categories, and among them are the following: cigarette; filter; glassine; food containers such as paper plates, cans, cups, and wrappers coated with plastic or aluminum foil to preserve flavor and texture, prevent contamination, or inhibit moisture; Sanfordized bag material called Clupak; vegetable parchment; wallpaper and surface-waxed paper. Papermakers are currently working with textile manufacturers to develop paper suitable for disposable surgical gowns and bed sheets. Specialties are now available in the synthetic-paper field.[19] Nonwoven "cloth" is now of considerable importance[20] for a wide variety of uses in the hospital, industry, and home. Many such materials contain plastics in addition to wood fibers. Costs are substantially lower than for conventional woven cloth.

STRUCTURAL BOARDS

The classification of boards[21] made from wood particles is not standardized in the United States, and the terms fiberboard, particleboard, flakeboard, and oriented board all frequently refer to particle boards.

Fiberboards are rigid and semirigid sheets formed by the wet- or dry-felting of fibers. The low-density kinds are generally used for insulation. The new medium-density types go mainly into furniture, and the high-density types into furniture and paneling. The fiber used is usually from soft- or hardwoods, cull timber, and mill residues, and the wood is pulped by mechanical, thermomechanical, or explosive processes. A small amount of adhesive, generally phenol-formaldehyde resin, is used—particularly with dry-felted boards. Treatment to improve flame resistance or water resistance or to protect against insect damage and rot is common.

Particleboard manufacture uses sawdust, shavings, and wood flakes of special shapes to combine good physical properties with attractive appearance. Synthetic resin adhesives and different pressing conditions give varying density, strength, and surface embossing. Boards with resin adhesives are high strength and can be made with predetermined engineering properties. They have their basic elements aligned substantially in one direction. Particleboards are used for subflooring, core stock for veneered furniture, and decorative paneling and are replacing plywood and lumber for some structural applications.

Paper-base laminates are multiple sheets of resin-treated paper bonded together under high pressure and heat; under these conditions they become rigid and have no characteristics of paper. Depending on the process used, these products are termed resin-filled or resin-impregnated. They possess several characteristics, such as stability and strength, among others, which make them useful in the building industry. Other types of polymer-modified materials are listed in Chap. 34.

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[19]Polymers Roll into Printing Paper Markets, *Chem. Eng.* 78 (6), 62 (1971); Bumpy Road Ahead for Synthetic Paper, *Chem. Eng. News* October 23, 1972, p. 13.

[20]Nonwovens Symposium, *Tappi* 58 (5) 38 (1975); Gould, *Specialty Papers*, Noyes, Park Ridge, N.J., 1976.

[21]Symposiums on Particleboard, Washington State University, 1970–1975.

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Chapter 6

Pharmaceutical Industry

The human lifespan in the United States has increased since 1900 from 49 years to the present 73+ years. This has been due, in part, to the development of drugs[1] that have controlled or eliminated many diseases that formerly were devastating in their action on humans. The death rate from influenza in the United States per 100,000 population dropped from 102.5 in 1930 to 26.7 in 1978, and from all forms of tuberculosis from 71.1 to 1.0 during the same period. Poliomyelitis has been practically eliminated by the advent of preventive vaccines.

HISTORICAL. The use of drugs to relieve pain and to ward off death is interwoven with the ancient superstition that evil spirits cause disease. The healing powers of mythological personages, particularly of Aesculapius, son of Apollo, were sought in primitive cultures. The Papyrus Ebers, which take us back to the beginning of recorded history in the Nile Valley, contain drug formulas with as many as 35 ingredients, including botanicals, minerals, and animal products. A few of the minerals, such as sulfur, magnesia, and soda, still appear in current pharmacopeias. It was the Greeks, Hippocrates and Galen, who made an effort to approach therapy rationally rather than mystically. Paracelsus, born in 1493, experimented both in the laboratory and the clinic, and may be looked upon as the founder of chemotherapy.

Three centuries later, while Liebig and his students in Germany were synthesizing biologically active compounds, methods for experimental medicine were developed in France by Bernard, Magendie, and others. Although the American pharmaceutical industry had made a modest beginning in 1786, the synthetic organic chemicals ether and chloroform were not used for anesthesia until the 1840s. Three years after the end of the Civil War, the first integrated industrial synthetic organic manufacturing operation was established in the United States.[2] The groundwork for modern pharmaceutical research was begun in 1881 with the establishment of a scientific division of Eli Lilly & Co. The shortage of important drugs, such as sedatives and novocaine, caused by the entry of the United States into World War I, precipitated expansion of the pharmaceutical industry into a successful effort to produce the synthetic chemicals needed.

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[1]The term "drugs" as used in this chapter refers to articles intended for use in the diagnosis, cure, alleviation, treatment, or prevention of disease in humans or animals; Oser (ed.), *Remington's Pharmaceutical Sciences*, vol. 16, 1980, hereinafter cited as RPS XVI.

[2]Albany Aniline Chemical Co. For this and other historical facts, see Tainter and Marcelli, The Rise of Synthetic Drugs in the American Pharmaceutical Industry, *N.Y. Acad. Med.* 35 387–405 (1959).

Developments of insulin, liver extract, and the barbiturates were milestones of the next decade. Sulfa drugs and vitamins were added to many product lines during the 1930s. Blood plasma, new antimalarials, and the dramatic development of penicillin resulted from the demands of war. The spectacular surge of new products, which included steroid hormones, tranquilizers, vaccines, and broad- and medium-spectrum antibiotics, came after World War II. The 1970s saw the exciting development of gene splicing to produce new forms of living materials.

USES AND ECONOMICS. The first law in the United States regulating drugs was the Food and Drug Act of 1906, but this act did not require advance testing of new drugs. In 1937 the use of ethylene glycol as a vehicle for sulfanilamide caused more than one hundred deaths and led to the 1938 amendment of the FD&C act. This amendment required proof of safety of any new drug *before* it was marketed. The advent of antibiotics led to the 1941 amendment which required certification of safety for each batch of antibiotic. The amendment of 1951 divided drugs into two categories—prescription and over-the-counter (OTC). Prescription drugs are those dispensed to the public by a licensed pharmacist upon the written order (prescription) of a licensed doctor, dentist, or veterinarian and include drugs deemed to be unsafe to be used indiscriminately. OTC drugs are offered for sale by pharmacists or other vendors without a prescription.

Other amendments further restricting the introduction of new drugs and regulating the use of hallucinogenic and narcotic drugs have been enacted. These laws have made the introduction of a drug that can cause deleterious effects upon humans or animals extremely unlikely. However, such safety has some undesirable consequences as it now requires more than seven years to develop and thoroughly test a new drug product. This procedure costs an average of $8 to $10 million. To acquire protection from competition the company developing a new drug must apply for a patent early in the process. Patents are valid for only 17 years, and if 7 years are subtracted for testing before the drug can be marketed, the company has only about 10 years of protection in which to try and recover its $8 million +. This has severely limited the number of new drugs introduced, and only those with a large potential market can be economically considered.[3] Four out of five new drugs never exceed $20 million per year in sales, and a law suit or two can kill the best of them. In 1980 12 new chemical entities were approved by the FDA. The longest remaining patent life was 11 years, 10 months, and 1 of the 12 had no patent protection remaining.

The total U.S. production of bulk medicinal chemicals has increased from 65,000 t in 1964 to 110,000 t in 1980.[3a] Sales of bulk products for 1964 were $643 million and in 1980 $1153 million. These figures do not include finished preparations, such as tablets, capsules, ampules, and the like, which manufacturing pharmacists make from bulk chemicals, antibiotics, and isolates. Antibiotics accounted for 22 percent; gastrointestinal agents, 27 percent; nervous system stimulants and depressants, 25 percent; and vitamins, 17 percent of the 1980 sales.[4] Product shipments in 1981 were valued at $1270 million. In 1981 the U.S. sales of OTC drugs was $5300 million.

The beneficent influence of the pharmaceutical industry on animals for human food is often not recognized. The control of animal diseases by drugs has cut the losses dramatically.

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[3]Burger, Behind the Decline in New Drugs, *Chem. Eng. News* 53 (38) 37 (1965); *Pharm. Mfr. Assoc.* newsletter 23 (31) 6 (1981).

[3a]t = 1000 kg.

[4]*Synthetic Organic Chemicals, 1980, Medicinal Chemicals*, U.S. International Trade Commission, 1981; *U.S. Industrial Outlook*, 1982, U.S. Department of Commerce.

In the early 1950s, American poultry producers suffered annual losses of birds of about 30 percent. Today the usual loss to disease is only about 1 percent. In addition, the use of vitamins, antibiotics, and steroids in animal and poultry feeds has greatly increased the amount of meat produced per unit of feed fed.

The pharmaceutical industry employs 144,800 people in 756 establishments. Of these companies, 463 employed less than 20 people each. The prescription pharmaceutical industry is not dominated by any one firm as can be seen from Table 6.2. The four largest companies accounted for 24 percent of the total. In 1981 the U.S. drug market was valued at $5770 million, and this constituted nearly 21 percent of the world market for drugs.

RESEARCH AND DEVELOPMENT. Members of the Pharmaceutical Manufacturer's Association (PMA), composed of 143 firms who account for approximately 95 percent of the prescription products sold in the United States, reported expenditures of over $1890 million for R&D for 1980, 24 times the amount expended in 1954 and 3 times that of 1970. Government support amounted to only $6.9 million. Research expenditures are a primary factor in determining a company's future share of industry sales and reflect the service rendered to the people. Figure 40.1 shows the R&D expenditures for several years.

CLASSIFICATION

Like most chemicals, pharmaceutical products can be arranged by use, by chemical structure, or by chemical reactions needed to manufacture the product.

Table 6.1 lists sales of OTC drugs and Table 6.2 lists the 50 most prescribed pharmaceutical products. These tables give an overall listing of many of the most useful pharma-

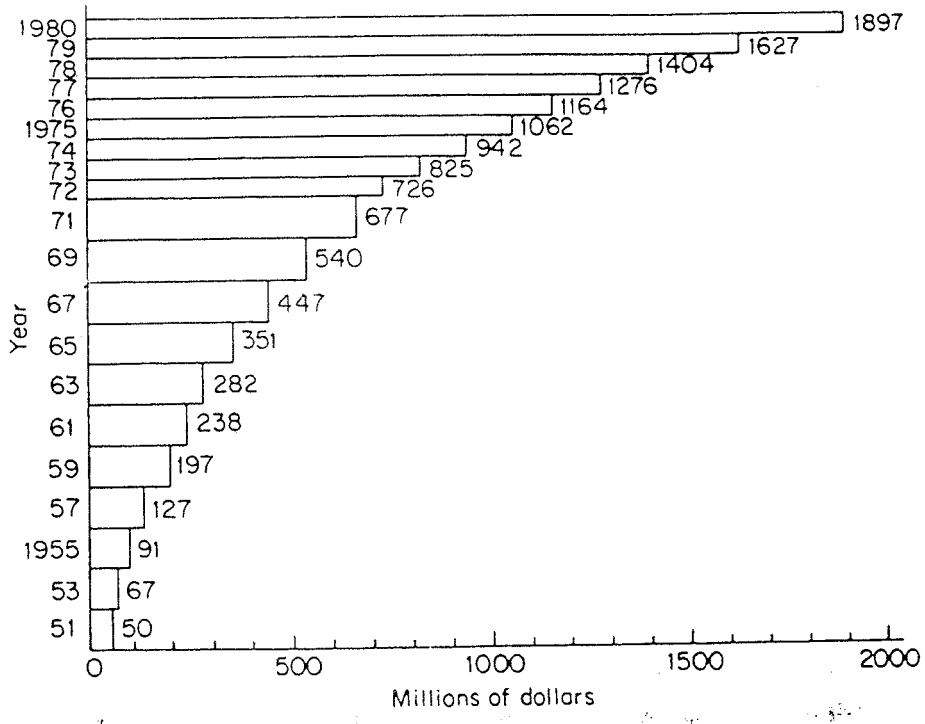

Fig. 6.1. Research and development expenditures for ethical products. *(PMA Annual Survey, 1979-1980.)*

***Table* 6.1** U.S. Retail Sales of OTC Pharmaceutical Products, 1978

	Sales, 10^6 $
Vitamins	950
Cold remedies	1010
Laxatives	360
Analgesics	
Internal	930
External	110
Nonsteroidal contraceptives	130
External antiseptics	120
Antacids	460
Others (burn, eye and contact lens solutions, sleep aids, etc.	1090
Total	4930

***Table* 6.2** Top 50 Most Prescribed Drugs in the United States in 1981

Rank 1981	Rank 1976	Trade Name	Generic Name	Manufacturer°	Therapeutic Class
1	1	Valium†	Diazepam	Roche	Antianxiety
2	16	Inderal†	Propanolol·HCl	Ayerst	Antianginal
3	3	Dyazide‡	Triamterene-hydrochlorothiazide	S K B	Antihypertensive
4	4	Tylenol/codeine	Acetaminophen-codeine phosphate	McNeil	Antipyretic
5	9	Lasix (oral)‡	Furosemide	Hoechst-Roussel	Diuretic
6	7	Motrin‡	Ibuprofen	Upjohn	Antiarthritic
7	16	Lanoxin	Digoxin	B-W	Digitolizer
8	18	Ampicillin‡	Ampicillin	Unspecified	Antibiotic
9	—	Tagamet‡	Cimetidine	S K B	Antiulcer
10	61	Tetracycline†	Tetracycline	Unspecified	Antibiotic
11	22	Penicillin VK	Penicillin VK	Unspecified	Antibiotic
12	35	Dalmane‡	Fluorazepam·HCl	Roche	Sedative
13	n.a.§	Dimetapp‡	Brompheniramine maleate-phenylephrine·HCl	Robins	Decongestant
14	2	Aldomet‡	Methyldopa	M S D	Antihypertensive
15	6	Keflex‡	Cephalexin	Dista	Antibiotic
16	n.a.	Amoxicillin‡	Amoxicillin	Unspecified	Antibiotic
17	8	Hydrochlorothiazide	Hydrochlorothiazide	Unspecified	Diuretic
18	15	Actifed	Triprolidene·HCl pseudoephedrine	B-W	Decongestant
19	83	E.E.S‡	Erythromycin	Abbott	Antibiotic
20	—	Darvocet-N100‡	Propoxyphene napsylate	Lilly	Analgesic
21	32	Erythromycin	Erythromycin	Unspecified	Antibiotic
22	—	HydroDiuril†	Hydrochlorothiazide	M S D	Diuretic
23	—	Slow-K‡	Potassium chloride	Ciba	Electrolyte
24	17	Premarin†	Conjugated estrogens	Ayerst	Estrogenic hormone
25	11	Indocin†	Indomethacin	M S D	Antiarthritic
26	23	Isordil‡	Isosorbide	Ives	Antianginal
27	25	Hygroton	Chlortholidone	USV	Antihypertensive

Table 6.2 Top 50 Most Prescribed Drugs in the United States in 1981 *(continued)*

Rank 1981	Rank 1976	Trade Name	Generic Name	Manufacturer*	Therapeutic Class
28	n.a.	V-cillin†	Penicillin	Lilly	Antibiotic
29	n.a.	Emperin-codeine	Aspirin-codeine phosphate	B-W	Antipyretic, analgesic
30	—	Synthroid	Levothyroxine Sulfate	Flint	Thyroid substitute
31	—	Clinoril‡	Sulindas	M S D	Antiarthritic
32	84	Donnatal†	Phenobarbital	Robins	Antispasmodic
33	40	Prednisone	Prednisone	Unspecified	Adrenocortical steroid
34	34	Dialantin sodium†	Phenytoin sodium	Parke Davis	Anticonvulsant
35	24	Diabinese‡	Chloropropamide	Pfizer	Hypoglycemic
36	19	Benadryl	Diphenhydramine	Pfizer	Antihistamine
37	45	Tranxene‡	Chlorazepate dipotassium	Abbott	Antianxiety
38	20	Amoxil‡	Amoxicillin trihydrate	Beecham	Antibiotic
39	84	Phenobarbital†	Phenobarbital	Unspecified	Sedative
40	—	Lopressor‡	Metoprolol tartrate	Geigy	Antihypertensive
41	71	Naprosyn‡	Naproxen	Syntex	Analgesic
42	5	Elavil	Amitriptyline·HCl	M S D	Antidepressive
43	48	Aldoril‡	Methyldopa-hydrochlorothiazide	M S D	Antihypertensive
44	13	Librium†	Chlorodiazepoxide	Roche	Antianxiety
45	—	Drixoral‡	Dexbromopheniramine maleate-pseudoephedrine sulfate	Schering	Antihistamine
46	30	Fiorinal†	Butalbitol-asprin	Sandoz	Analgesic
47	37	Thyroid	Thyroid	Unspecified	Hormone
48	—	Ativan‡	Lorazepam	Wyeth	Antianxiety
49	47	Antivert	Meclizine·HCl	Roerig	Antihistamine
50	66	Mycolog	Triamcinolone acetamide-gramicidin; neomycin sulfate, nystatin	Squibb	Corticoid steroid

*S K B, Smith Kline Beckman; B-W, Burroughs Wellcome; M S D, Merck, Sharpe & Dohme.

†In the first 50 since 1966.

‡Not in the first 200 in 1965.

§n.a.—not available.

SOURCE: *Pharmacy Times* April 1982.

ceuticals. Remington (RPS XVI) is helpful in presenting important drugs arranged by therapeutic class. In presenting the manufacturing of individual products, however, a chemical conversion classification is in accordance with the arrangement of the rest of this book and is consequently followed hereafter. The pharmaceutical industry employs greater variety and more complicated steps in its manufacturing processes than almost any other section of the chemical process industries. The complexity of the chemical structure of many medicaments probably has a relationship to the even greater complexity of the ailments of human and animal bodies which the products of the pharmaceutical industry are designed to ameliorate. Because of the accompanying complexity in manufacturing processes, it has been difficult to

select the important chemical-conversion step under which to classify the synthesis of an individual chemical.

In the pharmaceutical industry greater emphasis is placed upon the purity of the products than in most other chemical industries, except in certain cases in the nuclear industry (Chap. 21). Another characteristic of the pharmaceutical industry is the use of life processes as a step in the manufacture of some products which have assumed increasing importance in this area: antibiotics, biologicals, hormones, vitamins, and products of fermentation. Many of these pharmaceuticals are classified and presented under fermentation processes in this chapter, but the overall treatment of fermentation is found in Chap. 4. In the early centuries, a large proportion of the products used as medicaments were natural products, mostly derived from plants. It was recognized that such products must be pure, and, in the early decades of the modern pharmaceutical industry, much effort was devoted to separating and purifying the individual products extracted from plants or animals. Extractive methods have been improved by the use of equipment such as the Podbelniak contactor (Fig. 6.6), which allows countercurrent extraction to be performed efficiently and rapidly. This is essential for materials such as penicillin which are sensitive to time, temperature, and acidity. Specialized solvents, such as anhydrous ammonia, various alcohols, esters, and hydrocarbons are also important. Ion-exchange resins facilitate the extraction and purification of individual products such as antibiotics and alkaloids. Sterility and specialized packaging are necessary for many pharmaceuticals.

The U.S. Pharmacopeial Convention sets standards for purity of many prescription and OTC drugs. These standards are listed in the current volume of the U.S. Pharmacopeia, and drugs that meet these standards may use the designation USP. A few other drugs that are not as rigidly standardized are listed in the National Formulary, and drugs that meet these standards may use the letters NF. Many new drugs are not listed in either reference.

As a result of the great amount of research by pharmaceutical firms, many of the old drugs obtained by extraction of natural products have been supplanted by pure synthetic chemicals which may or may not be identical with the natural products. Certain individual drugs still prevail, however, such as morphine, codeine, and reserpine, extracted from plants, for which there is a continued demand on the part of physicians and for which no synthetic counterpart or substitute has been fully accepted.

Typical pharmaceutical products are presented from among the thousands manufactured by the industry and used by physicians. They are selected for inclusion in this chapter because of importance, volume produced, or illustrative processes.[5] They are arranged under their outstanding chemical conversion process or under fermentation.

ALKYLATION

PHENOBARBITAL USP.[6] Phenobarbital, 5-ethyl-5-phenylbarbituric acid, possesses specific usefulness in epilepsy. Like the other barbituric acid derivatives, it is made from phenylethylmalonic diethyl ester, which is condensed with urea to form the product.

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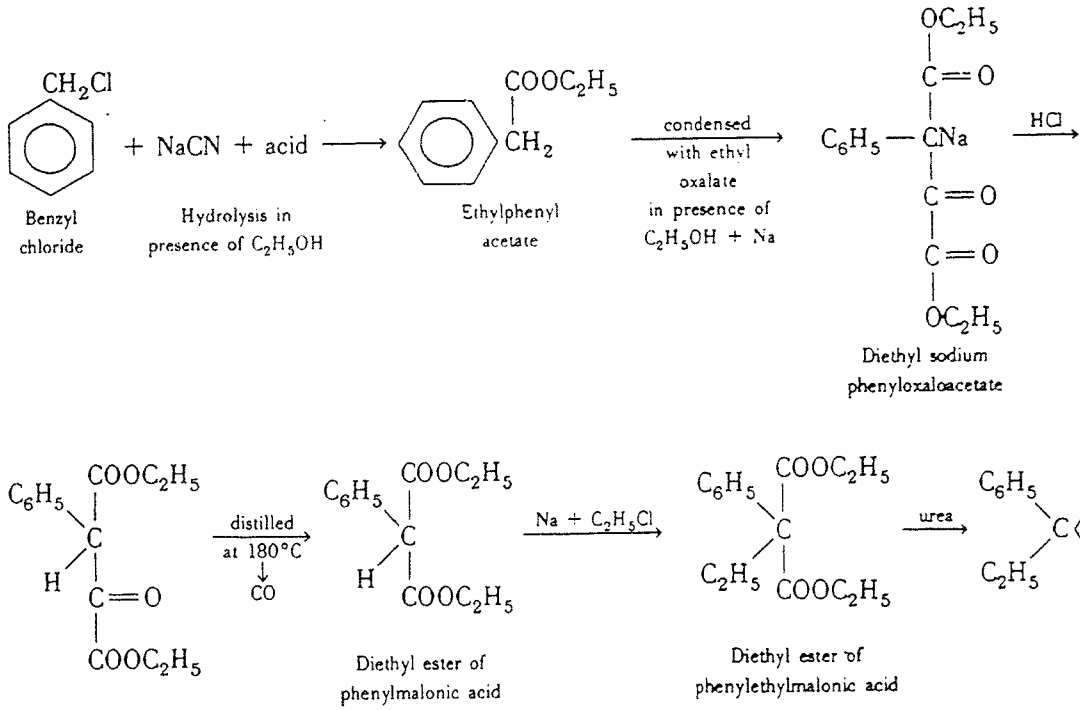
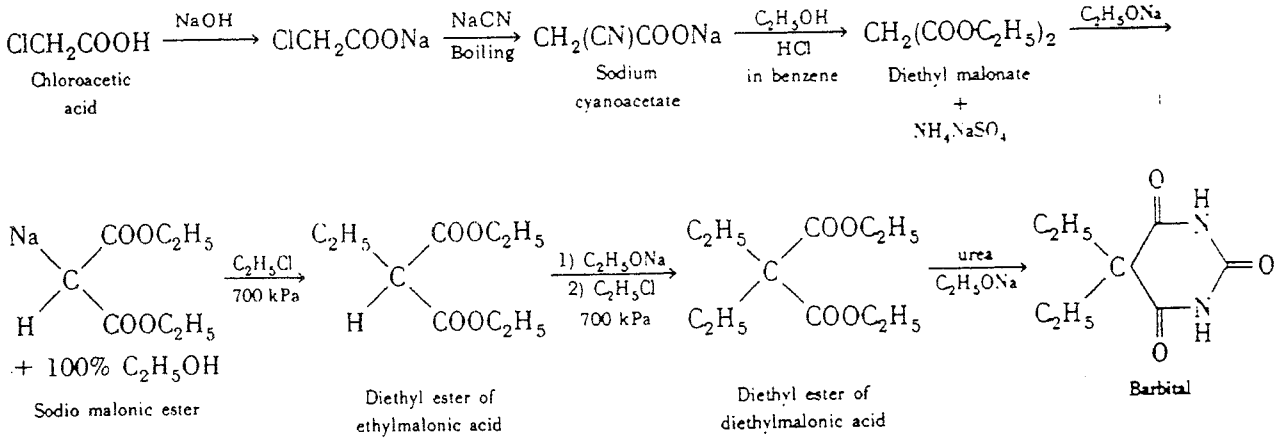
[5]RPS XVI gives the best overall short description of the thousands of pharmaceutical products actually employed, together with their various names, methods of production, and clinical properties. Further details can be found in Burger, *Medicinal Chemistry*, 4th ed., 2 vols., Wiley, New York, 1979–1981.

[6]RPS XVI, pp. 998–1003; ECT, 3d ed., vol. 14, 1981, p. 803.



BARBITAL. Barbital, diethylbarbituric acid, is sold under the trade name Veronal. It is the oldest of the long-acting barbiturates and is derived through diethyl malonate.[7]



PROCAINE HYDROCHLORIDE USP. This local anesthetic has long been dispensed under the name novocaine. It is considered to be less toxic than cocaine, and furthermore does not have the danger of habituation. It is used frequently in conjunction with a vasoconstrictor like epinephrine to secure a prolonged anesthetic action. It is obtained by first alkylating ethylenechlorohydrin with diethylamine, which is condensed with *p*-nitrobenzoyl chloride and reduced with tin and hydrochloric acid to obtain procaine.[8]

CODEINE NF AND CODEINE PHOSPHATE USP.[9] Codeine can be isolated from opium, and for many years the supply from this source was sufficient to meet the demand for this sedative

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[7]RPS XVI, p. 1011.

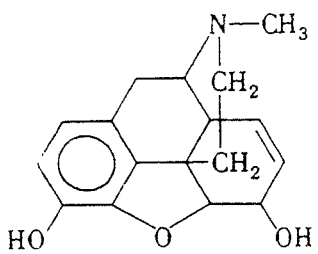
[8]RPS XVI, p. 996.

[9]RPS XVI, p. 1046; Groggins, *Unit Processes in Organic Synthesis*, 5th ed., McGraw-Hill, New York, 1958, p. 846.

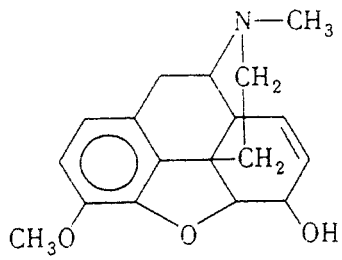
and analgesic drug. Currently demand far exceeds the supply from this source, but morphine (also obtained from opium, but in much larger amounts, 9 parts morphine to 1 part codeine) can be methylated to produce codeine. This is a difficult alkylation as there are three places in the morphine molecule to which a methyl group can be attached: alcoholic hydroxyl, phenolic hydroxyl, and tertiary nitrogen. To direct this alkylation to the phenolic hydroxyl and to reduce alkylation of the tertiary nitrogen, a quaternary nitrogen alkylating agent, phenyltrimethylammonium hydroxide, is employed. This results in yields of 90 to 93 percent codeine and some recovery of unalkylated morphine. The alkylation is carried out with the morphine dissolved in absolute alcohol in the presence of potassium ethylate. The dimethyl aniline and solvents are recovered and reused.

$$\text{morphine} + C_6H_5N(CH_3)_3OH + C_2H_5OK \xrightarrow[410\ kPa]{130°C} \text{codeine} + \underset{\text{Dimethylaniline}}{C_6H_5N(CH_3)_2} + C_2H_5OH + KCl$$

The basis of this reaction is morphine, which is obtained solely by isolation from opium, the dried exudate from the incised, unripe capsule of the opium poppy, *Papaver somniferum*. All the codeine that occurs in opium is isolated. See Morphine under Isolates. The relationship between morphine and codeine can be seen from the structural formulas.



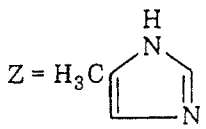
Morphine



Codeine (methylmorphine)

CIMETIDINE. Cimetidine, a highly substituted guanidine, is sold as Tagamet, and is widely used as an antiulcer medication.[10] Annual sales are about $400 million. It acts by blocking the histamine molecules in the stomach from signaling the stomach to secrete acid. Preparation is by the action of a substituted guanidine on an amino-thio compound in the presence of methyl cyanide.

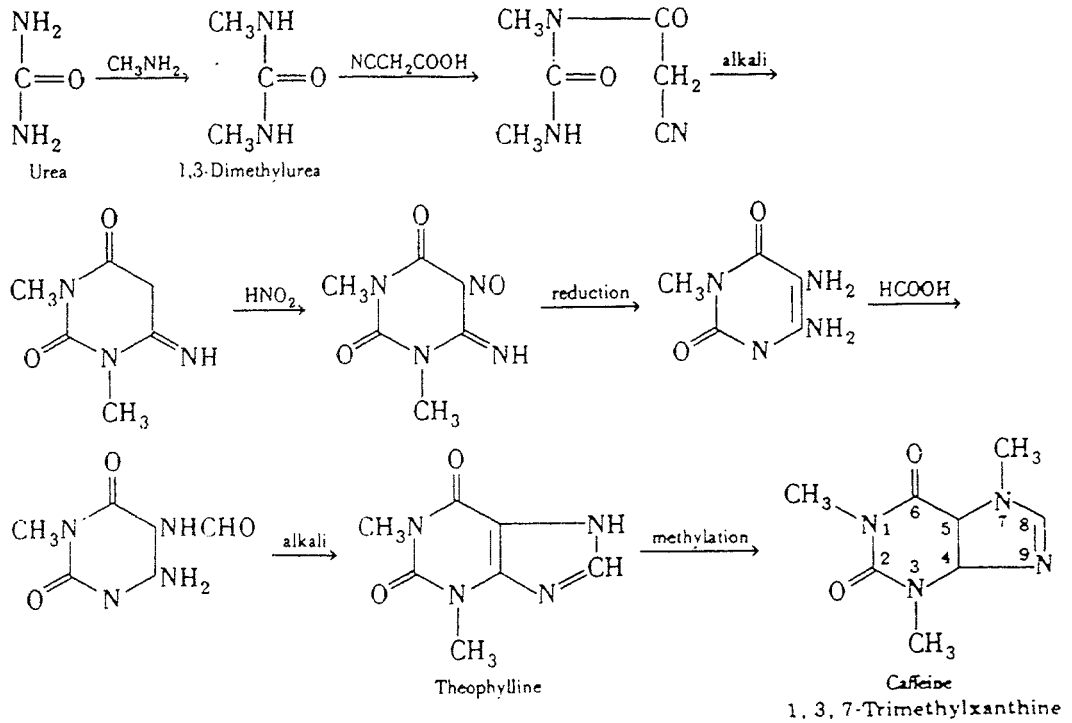
$$CH_3NHC(=NCN)SCH_3 + NH_2CH_2CH_2SCH_2Z \longrightarrow CH_3NHC(=NCN)NHCH_2CH_2SCH_2Z$$



CAFFEINE USP, THEOBROMINE NF, AND THEOPHYLLINE NF. Caffeine, theobromine, and theophylline are xanthine derivatives classified as central nervous stimulants, but differing

[10]RPS XVI, p. 754; New Drugs Tackle Ulcer Victims Excess Acid, *Chem. Eng. News* 60 (15) 24 (1982).

markedly in their properties. They can be extracted from a number of natural sources. Caffeine,[11] the most important, has long been obtained from waste tea and decaffeinization of coffee (see Caffeine under Isolates). The demand for caffeine is large in volume. Over 1.36 $\times$ 10^6 kg of caffeine are produced each year. It can be manufactured synthetically by a number of processes. Some have been employed industrially, for instance, the methylation of theobromine and also total synthesis by methylation and other reactions based upon urea. A typical sequence for the synthetic manufacture of caffeine is:



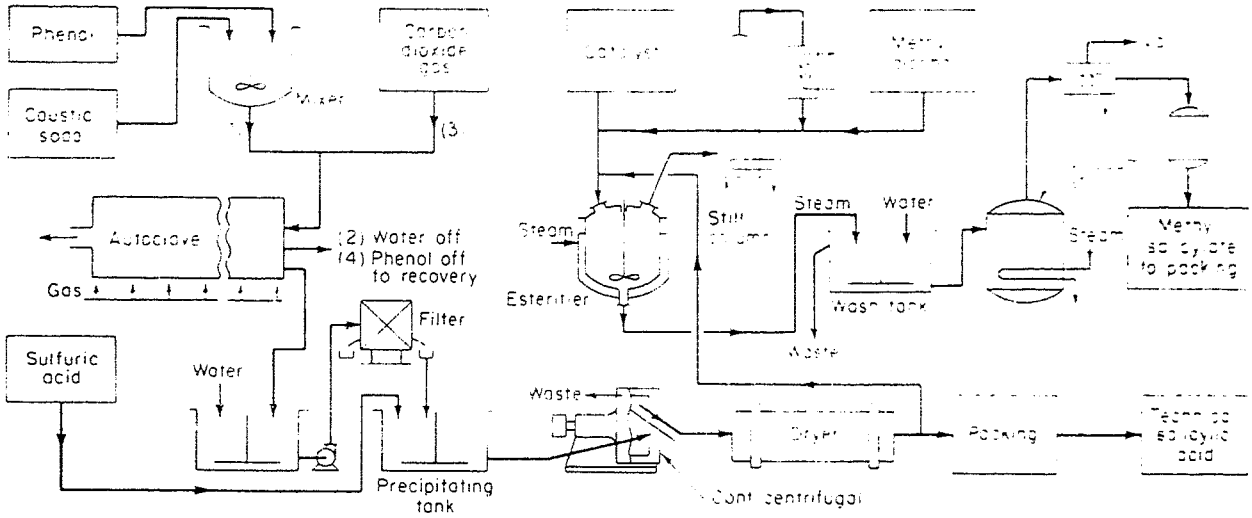
A large demand for caffeine comes from the pharmaceutical industry, but it is also used by the soft-drink industry for mildly stimulating beverages such as Coca Cola, Pepsi Cola, and the other cola drinks. A 600-ml bottle of Coca Cola contains only about one-third the amount of caffeine present in a 150-ml cup of coffee, and about the same amount as in a 150-ml cup of tea. Specifically, this amounts to 33 mg of caffeine in a 600-ml bottle of Coca Cola, whereas a 150-ml cup of tea contains 20 to 50 mg. A 150-ml cup of coffee has 65 to 150 mg.

CARBOXYLATION AND ACETYLATION

SALICYLIC ACID AND DERIVATIVES USP. The chief derivative of salicylic acid that is used as a drug is the methyl acetyl ester, which is known as aspirin. Yearly, over 22 $\times$ 10^3 t of the acid and 19 $\times$ 10^3 t of aspirin are produced. In 1981 the bulk price was $3.63 per kilogram. The manufacture of salicylic acid follows carboxylation by the Schmitt modification of the Kolbe reaction as shown in Fig. 6.2.[12]

[11]RPS XVI, p. 1076.

[12]*Chem. Eng. News* 60 (24) 7 (1982); RPS XVI, p. 1056; Sittig, *Pharmaceutical Manufacturing Encyclopedia*, Noyes, Park Ridge, N.J., 1979.



Reactions: $2C_6H_5OH + 2NaOH \longrightarrow 2C_6H_5ONa + 2H_2O$

$2C_6H_5ONa + CO_2 \longrightarrow ONaC_6H_4COONa + C_6H_5OH$

$ONaC_6H_4COONa + H_2SO_4 \longrightarrow OHC_6H_4COOH + Na_2SO_4$

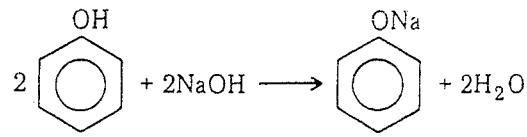
$OHC_6H_4COOH + CH_3OH \longrightarrow OHC_6H_4COOCH_3 + H_2O$

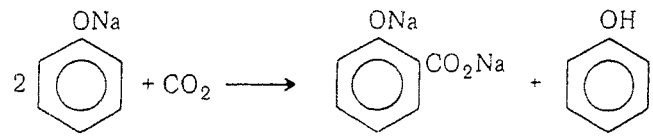
In order to produce 1 t of salicylic acid, the following materials (in kilograms) are required:

Phenol	800	Zinc	10
Caustic soda	350	Zinc sulfate	20
Carbon dioxide	500	Activated carbon	20

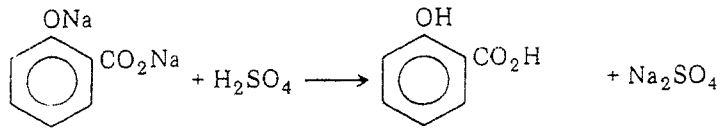
For the production of 1800 kg salicylic acid per day, 5000 kg of steam, 3600 MJ of power, and 53 work-h are required.

Fig. 6.2. Flowchart for salicylic acid and methyl salicylate

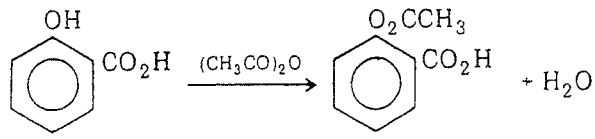




Sodium phenolate Sodium salicylate



Salicylic acid

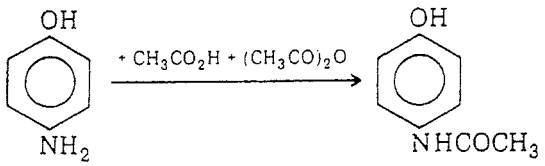


Aspirin

The sodium phenolate must be finely divided and exposed to the action of the CO_2 under pressure and heat. The equipment recommended for this process is a revolving heated ball mill[13] into which the sodium phenolate solution is introduced. By revolving under vacuum and heat (130°C), the sodium phenolate is reduced to a very dry powder, after which the CO_2 is introduced under pressure (700 kPa) and temperature (100°C) to form, first, sodium phenyl carbonate isomerizing to sodium salicylate. This can be dissolved out of the mill, and the salicylic acid decolorized by activated carbon and precipitated by adding sulfuric acid. The salicylic acid is purified by sublimation and can be esterified with methanol and a little sulfuric acid to form methyl salicylate if desired.

To form aspirin, the salicylic acid is refluxed with acetic anhydride in toluene at 88 to 92°C for 20 h. The reaction mixture is then cooled in aluminum cooling tanks, and the acetylsalicylic acid precipitates as large crystals. The crystals are separated either by filtration or centrifugation, washed thoroughly, and dried.

ACETAMINOPHEN USP.[14] Acetaminophen, sold under the tradename Tylenol, is a widely used analgesic and antipyretic that is an OTC drug. Combined with codeine it is one of the top five prescription drugs as shown in Table 6.2. Acetaminophen is prepared by treating *p*-aminophenol with a mixture of glacial acetic acid and acetic anhydride.



Acetaminophen

ACETOPHENETIDINE USP (PHENACETIN). Acetophenetidine, an analgesic and antipyretic, is the ethyl ether of acetaminophen and is prepared from *p*-ethoxyaniline.

CONDENSATION AND CYCLIZATION

The binding together of several molecules by condensation or ring closure to cause cyclization, with or without the splitting out of a smaller molecule, is a very important process employed in the manufacture of a considerable number of pharmaceutical products.

DIAZEPAM USP (VALIUM).[15] Diazepam is a substituted benzodiazepine made by a complex series of reactions, one of which involves cyclization. This compound was introduced between 1955 and 1960, and today is the most prescribed drug in the United States. It is an antianxiety drug, often called a tranquilizer. It is prepared by treating *p*-chloromethylaniline with benzoyl chloride and hydroxylamine to produce the benzophenone oxime. Reaction of the oxime with chloroacetyl chloride in the presence of sodium hydroxide and subsequent reduction yields diazepam.

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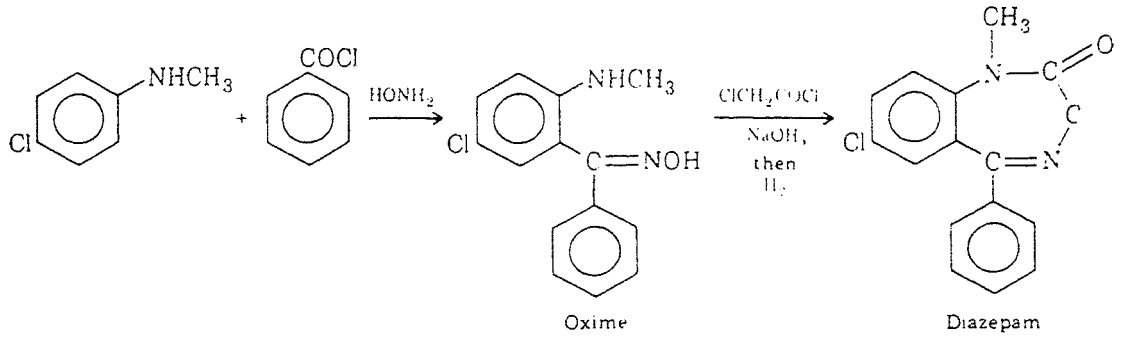
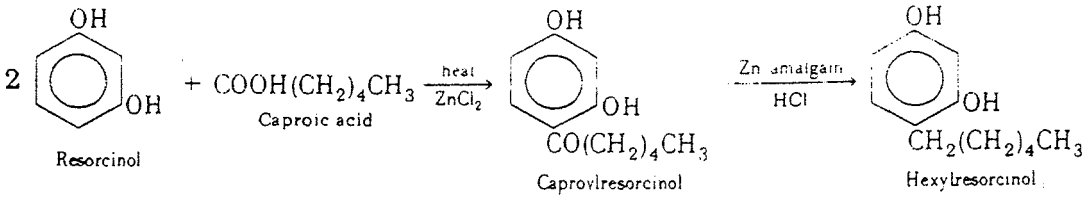
[13]For ball-mill reactor details see Groggins, op. cit., p. 367.

[14]Lednicer and Mitscher, *The Organic Chemistry of Drug Synthesis*, Wiley, New York, 1977.

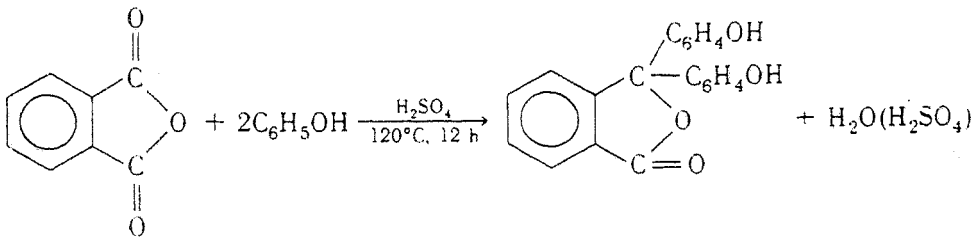
[15]RPS XVI, p. 1007; ECT, 3d ed., vol. 13, 1981, p. 127.



HEXYLRESORCINOL USP (1,3-DIHYDROXY-4-HEXYLBENZENE). Hexylresorcinol has marked germidical properties, and a phenol coefficient of over 50. It is a valued odorless and stainless antiseptic commonly employed in a dilution of 1:1000. It is one of the most efficient anthelmintics against hookworm and the like. In the manufacture of hexylresorcinol,[16] resorcinol and caproic acid are heated with a condensing agent, such as zinc chloride, and the intermediate ketone derivative is formed. This compound is purified by vacuum distillation. After reduction with zinc amalgam and hydrochloric acid (Clemmensen's reduction), impure hexylresorcinol is formed, which can be purified by vacuum distillation. Hexylresorcinol and its analogues were one of the series of related chemicals exhaustively studied to ascertain the relationship between chemical constitution and bactericidal power. It was found that this action increased up to the hexyl derivative and disappeared with the normal octyl derivative, probably because of low solubility. Figure 6.3 plots the atomic weight of the alkyl chain against the phenol coefficient (ratio of antibacterial power measured against the organism *Eberthella typhosa* relative to that of phenol under the same conditions). Simultaneously, with the increase in bactericidal power up to the hexyl derivative, a coincident drop in toxicity was found. Compare Table 40.3 on germicidal activity.



PHENOLPHTHALEIN NE.[17] Phenolphthalein is a widely used cathartic, particularly in proprietary drugs. It is manufactured by adding melted phenol (10 parts) to a cooled solution of phthalic anhydride (5 parts) in concentrated sulfuric acid (4 parts) and heating the mixture 10 to 12 h at 120°C. The hot condensation product is poured into boiling water and boiled with successive changes of hot water. The condensate is then dissolved in warm, dilute caustic soda and precipitated with acetic acid. It may be purified by crystallization from absolute alcohol after treatment with, and being filtering through, activated carbon.



[16]Groggins, op. cit., p. 839; RPS XVI, p. 1181.

[17]RPS XVI, p. 743.

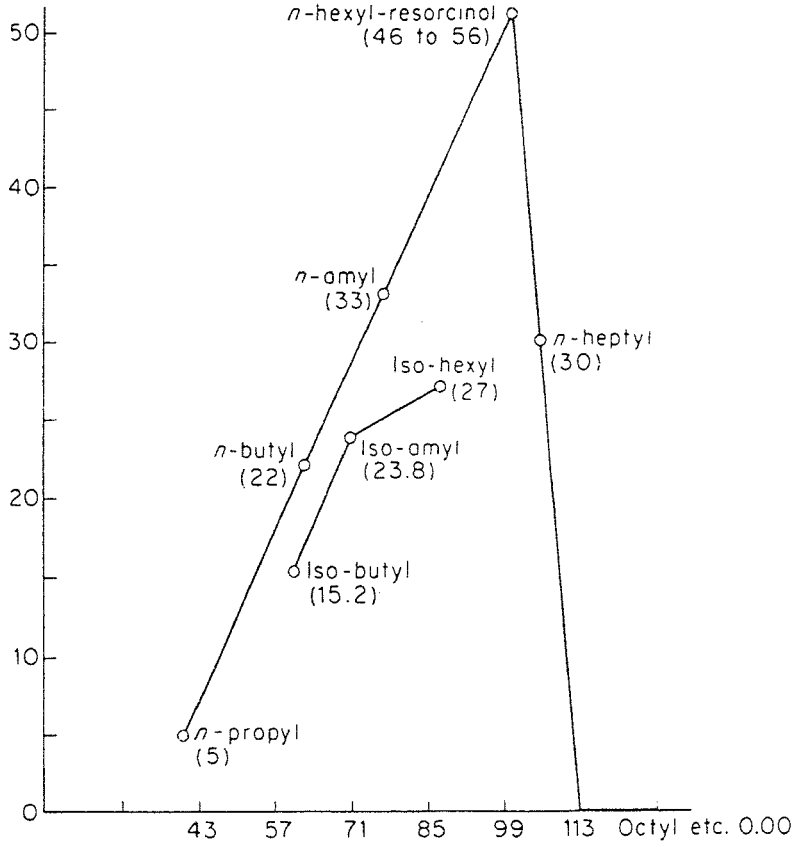
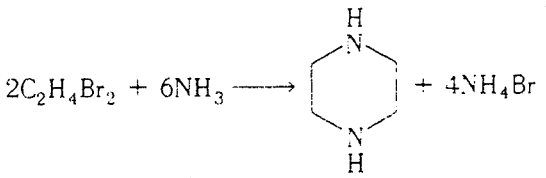


Fig. 6.3. Bacterial activity of the alkylresorcinols. The curve is obtained by plotting the phenol coefficients (U.S. Hygienic Laboratory technique) as ordinates against the sum of the atomic weights of the atoms in the alkyl chains as abscissas. [*Dohm, Cox, and Miller, J. Am. Chem. Soc.*, 48 *1688 (1962); Groggins, Unit Processes in Organic Synthesis, 5th ed., McGraw-Hill, New York, 1958, p. 389.*]

PIPERAZINE CITRATE USP.[18] Piperazine citrate is used as an anthelmintic in the treatment of infections caused by pinworms and roundworms. It is also employed by veterinarians against various worms infecting domestic animals, including chickens. The U.S. International Trade Commission reported production in 1980 of 1.8×10^3 t and a sales value of about $6.5 million. Piperazine is prepared by the cyclization of ethylene dibromide with alcoholic ammonia at 100°C. The citrate is formed in aqueous solution and crystallized out.



THIAMINE HYDROCHLORIDE USP, VITAMIN B_1.[19] This antineuritic vitamin is essential for bodily growth and the prevention of beriberi. Although thiamine is widely distributed in many foods, most commercially available quantities are obtained by the condensation of 6-amino-5-bromomethyl-2-methylpyrimidine hydrobromide with 5-(hydroxytethyl)-4-meth-

[18]RPS XVI, p. 1182.

[19]RPS XVI, p. 968.

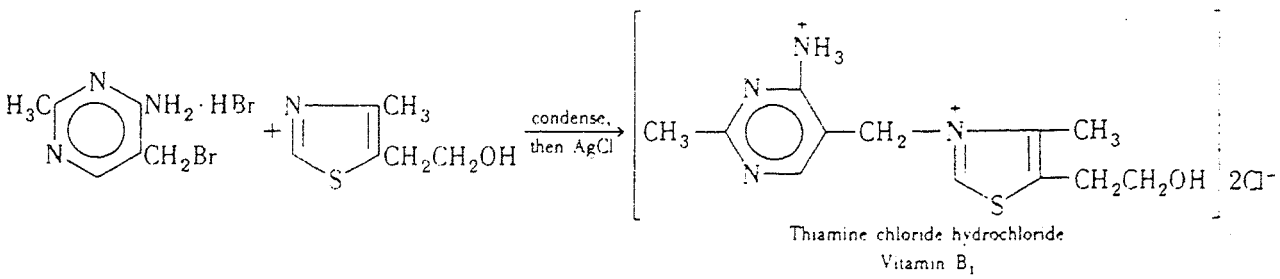
Table 6.3 Germicidal Activity of Certain Disinfectants in the Presence of Organic Matter

Disinfectant	*Eberthella typhosa*				*Staphylococcus aureus*			
	No Organic Matter Added		With 10% of Horse Blood		No Organic Matter Added		With 10% of Horse Blood	
	Effective Dilution	Phenol Coefficient	Effective Dilution	Phenol Coefficient	Effective Dilution	Phenol Coefficient	Effective Dilution	Phenol Coefficient
Phenol	1:90	1.0	1:80	0.9	1:60	1.0	1:50	0.8
Cresol compound USP	1:180	2.0	1:90	1.0	1:90	1.5	1:50	0.8
Cresylic disinfectant (stated phenol coefficient 5)[a]	1:500	5.5	1:150	1.6	1:250	4.1	1:70	1.1
Fortified cresylic disinfectant (stated phenol coefficient 5)[b]	1:500	5.5	1:150	1.6	1:250	4.1	1:70	1.1
Orthophenylphenol 15% disinfectant (Saponaceous)	1:600	6.6	1:120	1.3	1:200	3.3	1:20	0.3
Synthetic phenolic disinfectant (stated phenol coefficient 10)[c]	1:950	10.5	1:150	1.5	1:300	5.0	1:35	0.5
4-Chlorophenylphenol 8% disinfectant[d]	1:500	5.5	1:80	0.9	1:700	11.6	1:12	0.2
Pine oil disinfectant (stated phenol coefficient 4)[e]	1:225	2.5	1:250	2.7	1:20	0.3	1:20	0.3
Chlorine disinfectant I[f]	1:130	1.4	0	0	1:110	1.8	0	0
Chlorine disinfectant II[g]	1:600	6.6	1:3	0.03	1:400	6.6	1:1	0.01
Quaternary ammonium disinfectant I[h]	1:12,000	133	1:70	0.8	1:20,000	333	1:3,500	58
Quaternary ammonium disinfectant II[i]	1:27,000	300	1:3,000	33	1:10,000	166	1:4,500	75

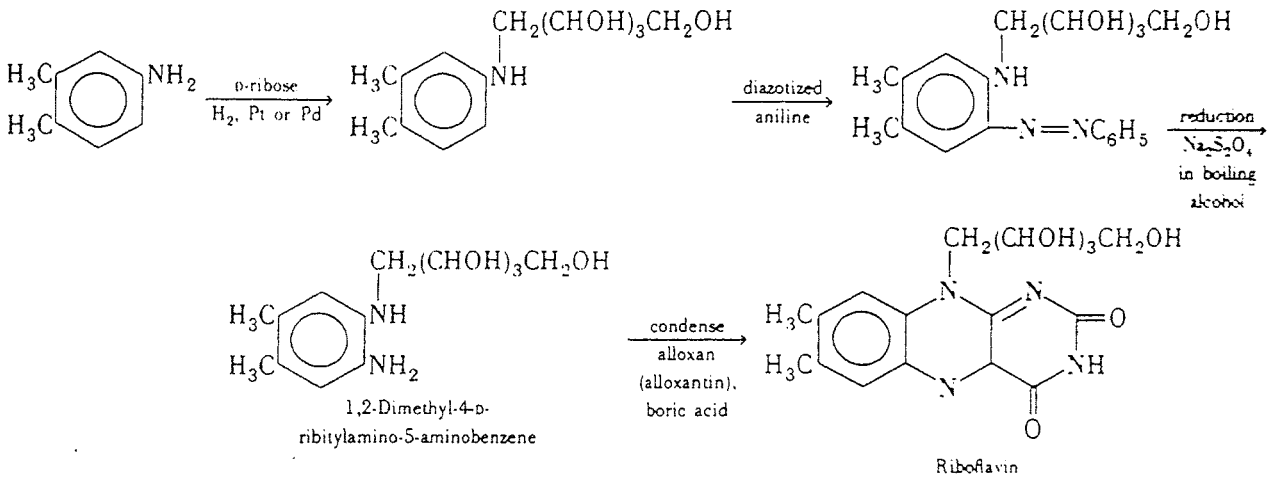
Nature of tabulated disinfectant: [a]51% cresylic acid solubilized by soap; [b]26% cresylic acid, 9% *o*-phenylphenol solubilized by soap; [c]10% *o*-phenylphenol, 4% *p*-tert-amylphenol solubilized by soap; [d]8% solubilized by soap; [e]76% pine oil solubilized by soap; [f]0.48% average chlorine; [g]5.25% average chlorine; [h]hydroxydecenyldimethylethyl ammonium bromide; [i]benzalkonium chloride, aqua.

SOURCE: *Soap Sanit. Chem.*, February 1944, has more details and more extensive tables.

ylthiazole, which results in thiamine chloride hydrochloride. The last step is:



RIBOFLAVIN USP, VITAMIN B_2.[20] Riboflavin is a necessary element of all living cells. It is quite stable except under excessive exposure to light. It is considered to be the growth factor of the vitamin B_2 complex and is added on a large scale to bread, flour, and other dietary and pharmaceutical preparations. It is also involved in the transfer of oxygen to tissues. This vitamin is produced as a by-product of the butanol-acetone fermentation of molasses and by synthesis starting with 1,3,4-xylidine, D-ribose, aniline, and alloxan.



DEHYDRATION

ETHER USP. Ether is used for general anesthesia and as a solvent. Ether and nitrous oxide, both anesthetics, are manufactured through dehydration reactions. The very simple and long-used manufacturing procedure for ether has been the dehydration of alcohol (denatured with ether) by sulfuric acid. The anesthetic ether is especially purified and packaged. Much ether, both USP and commercial grades, is now supplied as a by-product from the manufacture of alcohol from ethylene (see Chap. 38).

HALOGENATION

Halogenation, generally chlorination, is used extensively as a chemical step in the manufacture of various intermediates, such as ethyl chloride or bromide, and homologs employed in

[20]RPS XVI, p. 961; *McGraw-Hill Encyclopedia of Science and Technology*, 5th ed., vol. 11, McGraw-Hill, New York, 1982, p. 652.

in the manufacture of finished pharmaceutical products. In only a few cases does the chlorine remain in the finished product. One such compound is chloroform. Chloroform was once employed as an anesthetic by inhalation, but now is used only rarely in the United States. It is used as a solvent for alkaloids and other organic chemicals, in chemical analysis, and as a preservative during aqueous percolation of vegetable drugs, preventing bacterial decomposition.

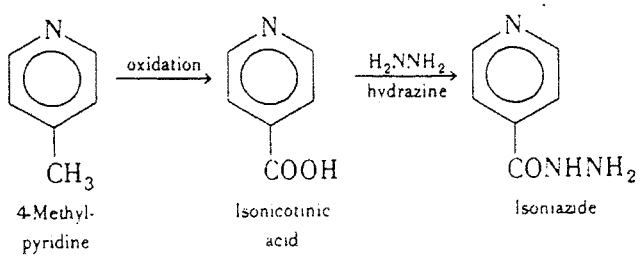
CHLOROFORM USP.[21] Although alcohol and chlorinated lime were formerly used to make chloroform, it is now made from acetone and calcium hypochlorite because the reaction is more rapid and the yield is high.

$$\underset{\text{Acetone}}{2CH_3COCH_3} + \underset{\substack{\text{Calcium}\\\text{hypochlorite}}}{3Ca(OCl)_2} \rightarrow \underset{\text{Chloroform}}{2CHCl_3} + \underset{\substack{\text{Calcium}\\\text{acetate}}}{Ca(C_2H_3O_2)_2} + \underset{\substack{\text{Calcium}\\\text{hydroxide}}}{2Ca(OH)_2}$$

Absolutely pure chloroform decomposes readily on storing, particularly if exposed to moisture and sunlight, to yield phosgene and other compounds. The USP requires the presence of a small amount of alcohol to retard this decomposition (0.5 to 1%).

OXIDATION[22]

ISONIAZID USP. Isoniazid, isonicotinic acid hydrazide, is the most potent and selective of the tuberculostatic antibacterial agents.



NICOTINIC ACID USP AND NICOTINAMIDE USP. Nicotinic acid and nicotinamide are known as niacin and niacinamide in the food industry. Niacin is the most stable of all vitamins and is essential to humans and animals for growth and health. In the body, niacin is converted to niacinamide, which is an essential constituent of coenzymes I and II, which are involved in the oxidation of carbohydrates. It is often added to foods, as in enriched flour. Niacin and niacinamide are nutritionally equivalent, and compete with one another. In the past methylethylpyridine was oxidized with nitric acid to yield niacin, and β-picoline was treated with air and ammonia to produce the nitrile which was then hydrolyzed to niacinamide. A new process can produce both niacin and niacinamide from a single feedstock, either β-picoline or 2-methyl-5-ethylpyridine by oxidative ammonolysis, a combination of oxidation and amination.[23]

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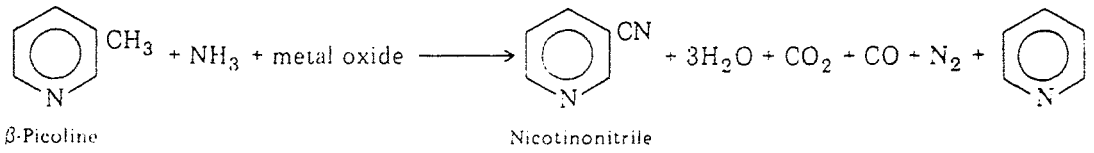
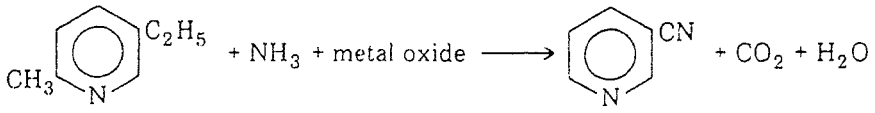
[21]RPS XVI, p. 1259.

[22]Groggins, op. cit., pp. 486–554.

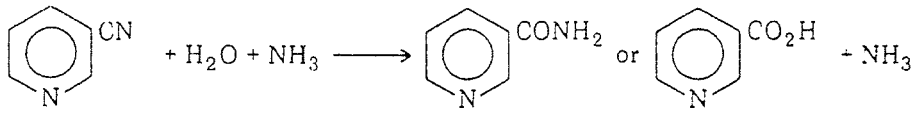
[23]Paustian, Puzio, Stavropoulos, and Sze, A Lesson in Flow Sheet Design; Nicotinamide and Acid, *CHEMTECH* 11 (3) 174 (1981).



β-Picoline Nicotinonitrile



2-Methyl-5-ethyl-pyridine Nicotinonitrile

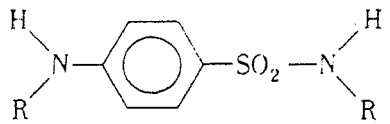


Niacinamide Niacin

Either the acid or niacinamide can be selectively isolated from the hydrolysis by varying the hydrolysis time and nitrile concentration. Production of niacin is favored by a higher hydrolysis temperature.

SULFONATION[24]

The outstanding drugs made by sulfonation are sulfanilamide, sulfadiazine, sulfaguanidine, and sulfathiazole. Sulfanilamide, the original member of this class, is a very interesting chemical, long known as an intermediate in the manufacture of an orange-colored dye, Prontosil, before its antibacterial properties were recognized.[25] It was ascertained in 1935 that sulfanilamide (*p*-aminobenzenesulfonamide) was the active antimicrobial part of the dye. About 3300 sulfonamides have been synthesized, but only a few have passed the careful testing of the pharmaceutical industry and clinicians. The following structure characterizes all therapeutically useful sulfanilamides:



The sulfa drugs have been largely replaced by antibiotics because the sulfas have relatively narrow antibacterial spectra, comparatively low potency, and cause rapid development of resistant organisms and many adverse side effects in humans. They are often used as diuretics.

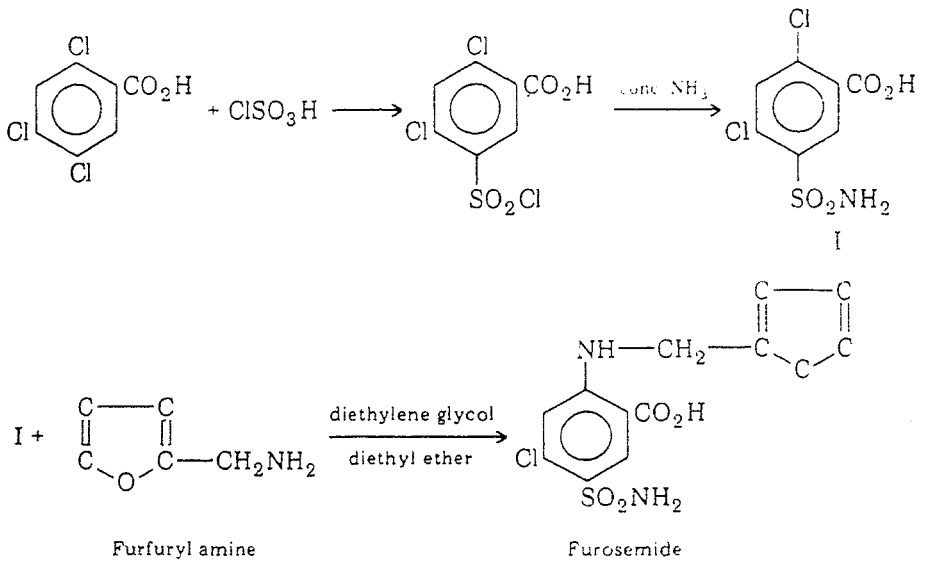
FUROSEMIDE.[26] Furosemide, 4-chloro-N-furfuryl-5-sulfamoyl anthranilic acid, is prepared by treating 2,4,5-trichlorobenzoic acid with chlorosulfonic acid, and further treatment with

[24]Groggins, op. cit., pp. 303–389; Gilbert, *Sulfonation and Related Reactions*, Interscience, New York, 1965.

[25]RPS XVI, p. 1116.

[26]RPS XVI, p. 883; Sittig, op. cit., p. 295.

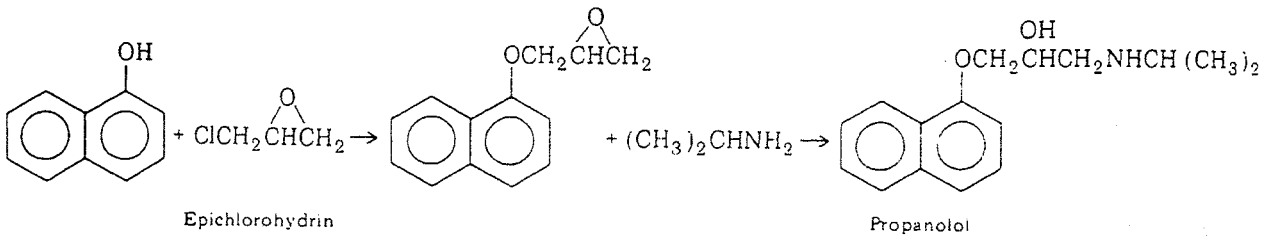
ammonia and furfuryl amine. This is a very potent diuretic and was the fifth most prescribed medicine in 1981.



AMINATION[27]

Many chemicals used as drugs contain one or more amine groups. These may be introduced into the compound by using ammonia or an amine.

PROPANOLOL·HCl.[28] This compound, sold under the tradename Inderal, was the second most widely prescribed drug in 1981. It is used as an antianginal and antihypertensive drug and is prepared from 1-naphthol and epichlorohydrin. Subsequent treatment with isopropyl amine opens the epoxy ring to yield propanolol. Treatment with HCl yields the hydrochloride.



COMPLEX CHEMICAL CONVERSIONS

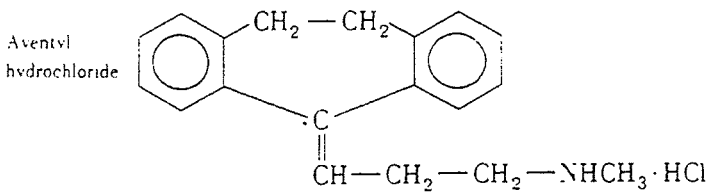
Many pharmaceutical chemicals are subjected to repeated, and often difficult, chemical reactions in order to obtain the desired product. Such conversions may be exemplified by ascorbic acid, chloramphenicol, and Aventyl HCl.[29] The latter, as an antidepressant, demonstrates this complex development. Twenty-six different chemicals are required to place the drug's 43 atoms in their precise molecular pattern in a six-step manufacturing process starting from

[27]Groggins, op. cit., pp. 388–485.

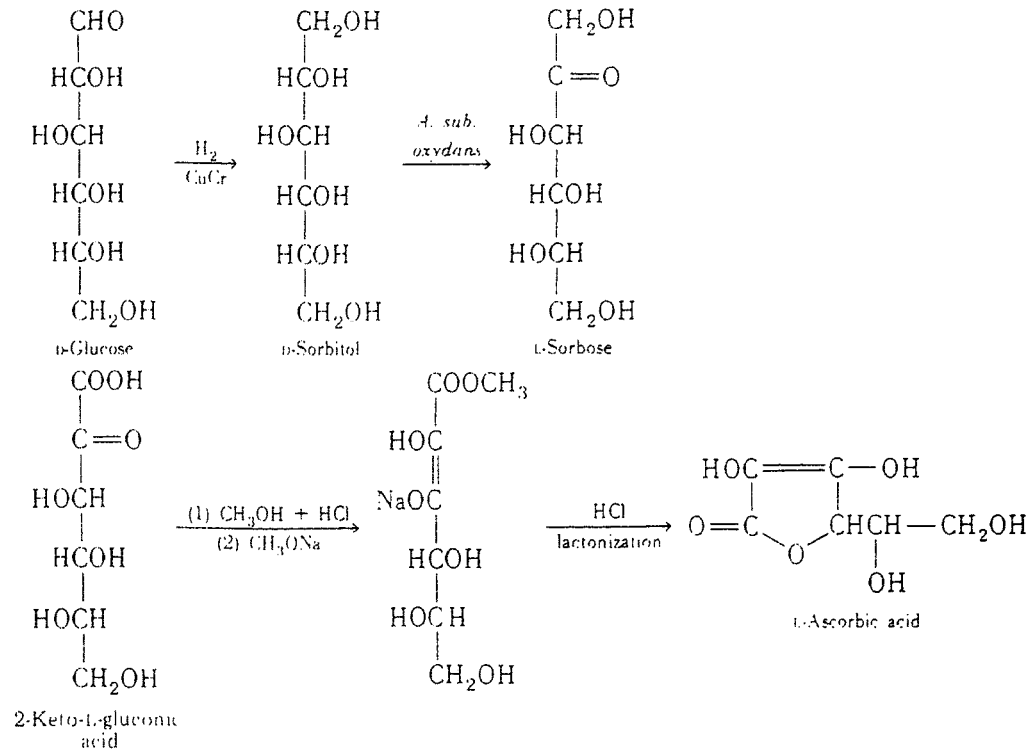
[28]RPS XVI, p. 845; Lednicer and Mitscher, op. cit., p. 117.

[29]Peters and Hennion, Synthesis of Nortriptyline, *J. Med. Chem.* 7 390 (1964).

phthalic anhydride. Its formula is



ASCORBIC ACID USP, VITAMIN C.[30] Vitamin C is often called the antiscorbutic vitamin. It is also needed in wound and bone healing and is a factor in resisting infection. Much of this vitamin is supplied in foods, especially fresh citrus fruits, tomatoes, and green vegetables. Ascorbic acid in solution or in foods is unstable, but the contrary is true if it is in dry form (powder or tablets). All the ascorbic acid used commercially is synthesized; 14.5×10^3 was produced in 1981. It is produced from glucose by these reactions:



DARVON. Darvon (Lilly), *d*-propoxyphene HCl, is a synthetic, nonantipyritic, orally effective analgesic, similar pharmacologically to codeine. "It is approximately equal milligram for milligram to codeine in analgesic potency, produces no respiratory depressions, and has little or no antitussive activity."[31] It is unique in that it is not a narcotic yet can be substituted for codeine, and is useful in any condition associated with pain. This analgesic is not analogous *chemically* to codeine or morphine. It was discovered and synthesized commercially in the Lilly laboratories. Its synthesis starts with relatively simple chemicals, but many steps are involved in its manufacture. These are outlined in the following *chemical conversions*. The second step is detailed and illustrated in Fig. 6.4.

[30]RPS XVI, p. 995; *McGraw-Hill Encyclopedia of Science and Technology*, 5th ed., vol. 1, McGraw-Hill, New York, 1982, p. 745.

[31]RPS XVI, p. 1061; Lednicer and Mitscher, op. cit., p. 50.

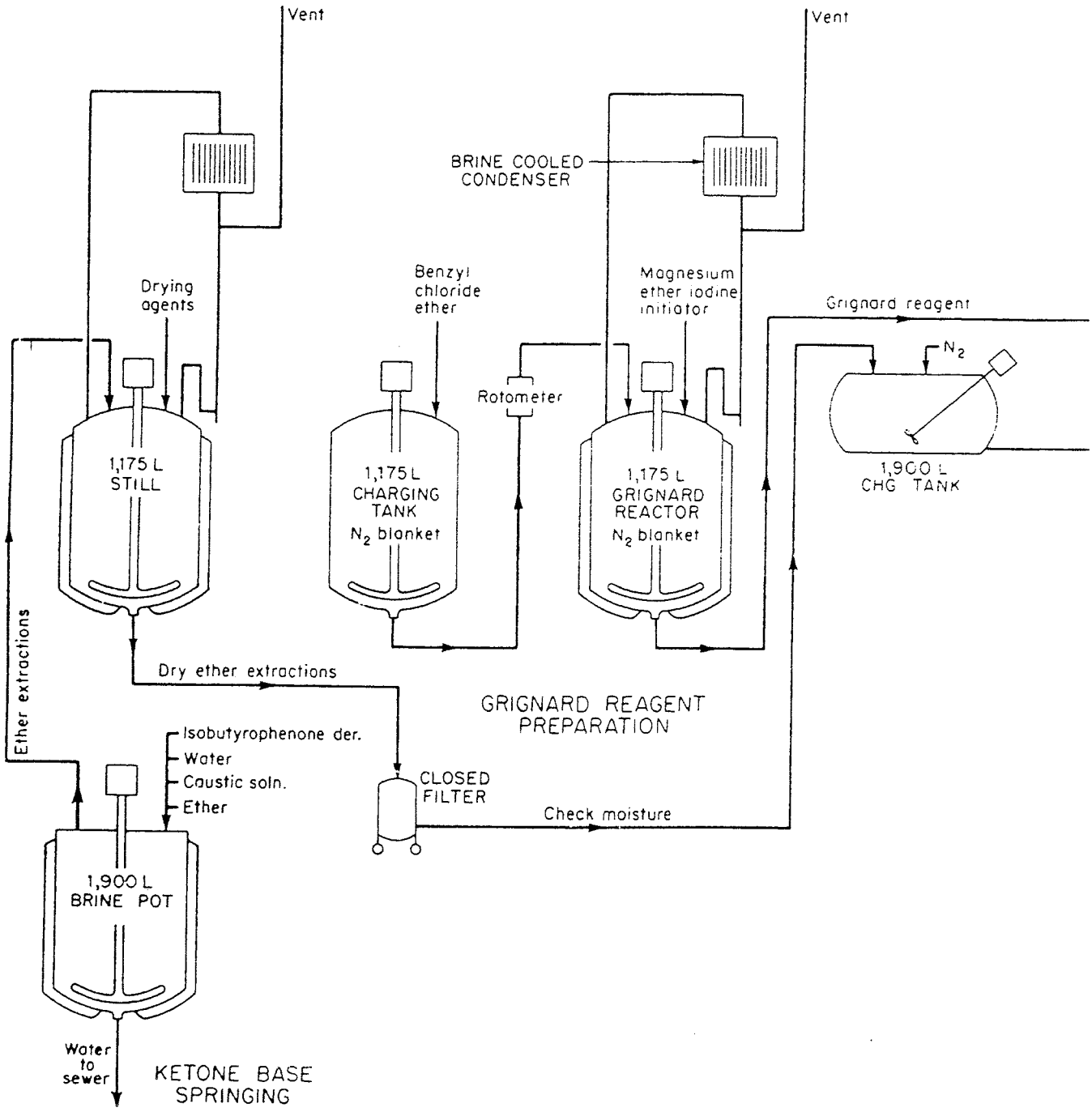
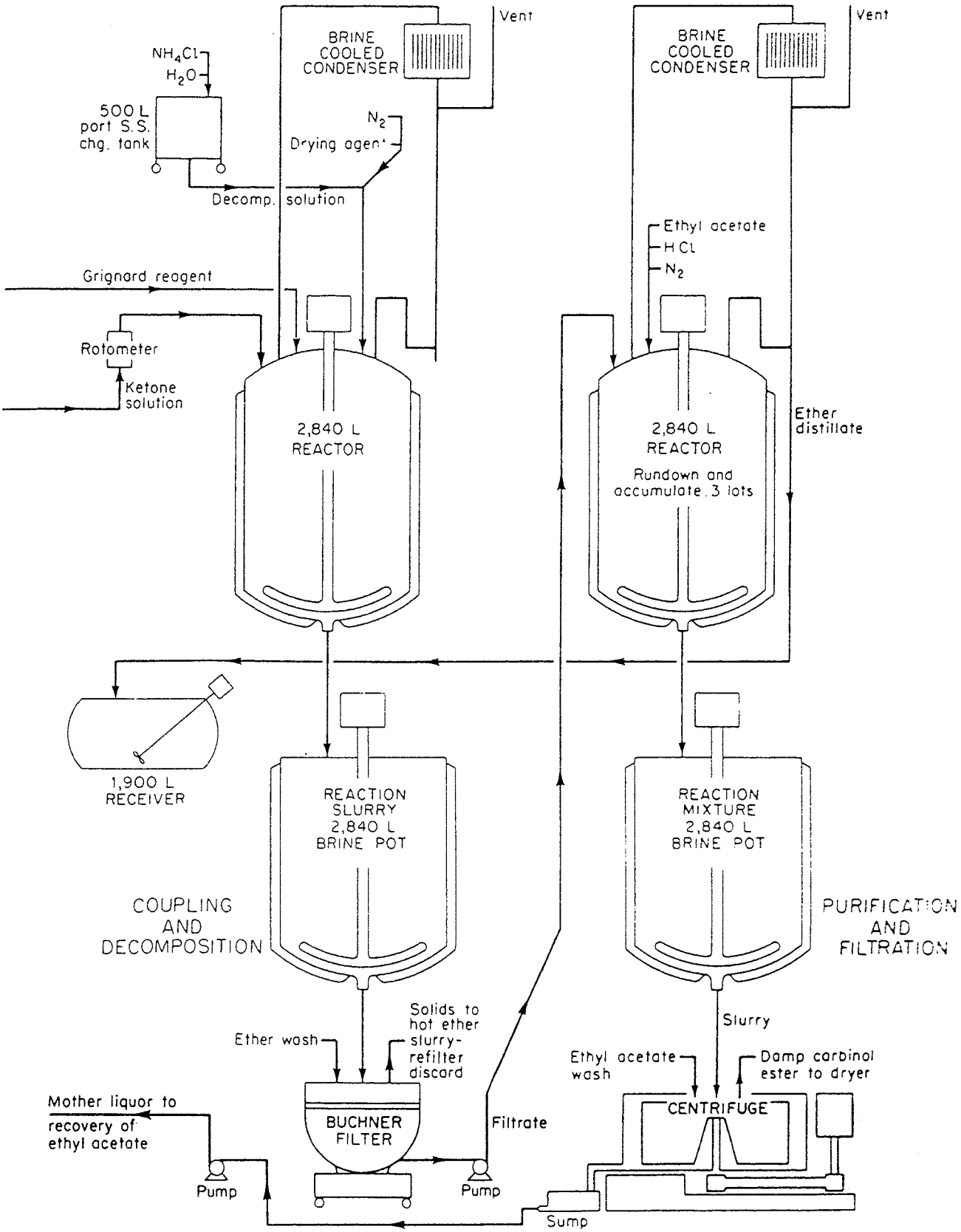
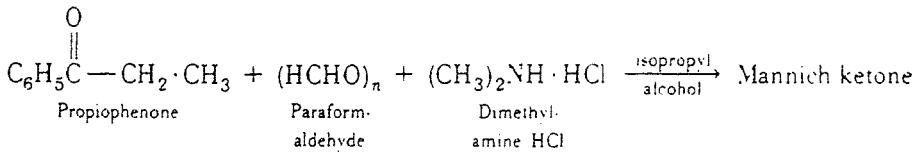


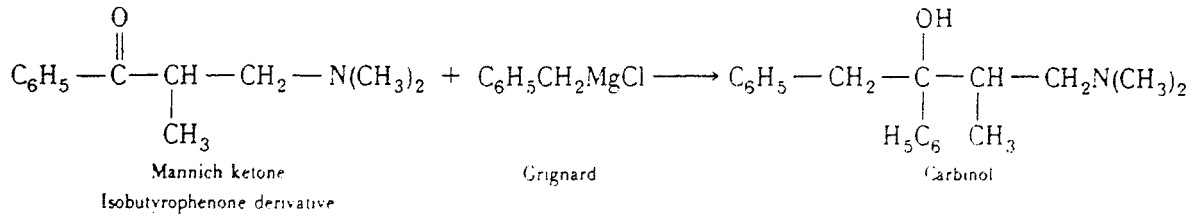
Fig. 6.4. Darvon production flowchart, showing equipment involved in step 2 described in the text. *(Eli Lilly & Co.)*


BRINE COOLED CONDENSER
Vent
BRINE COOLED CONDENSER
Vent
NH_4Cl
H_2O
500 L port S.S. chg. tank
N_2
Drying agent
Decomp. solution
Ethyl acetate
HCl
N_2
Grignard reagent
Rotometer
Ketone solution
2,840 L REACTOR
2,840 L REACTOR
Rundown and accumulate 3 lots
Ether distillate
1,900 L RECEIVER
REACTION SLURRY 2,840 L BRINE POT
REACTION MIXTURE 2,840 L BRINE POT
COUPLING AND DECOMPOSITION
PURIFICATION AND FILTRATION
Solids to hot ether slurry-refilter discard
Ether wash
Slurry
Ethyl acetate wash
Damp carbinol ester to dryer
Mother liquor to recovery of ethyl acetate
BUCHNER FILTER
Filtrate
CENTRIFUGE
Pump
Pump
Sump

Step 1. Coupling to give a Mannich ketone.



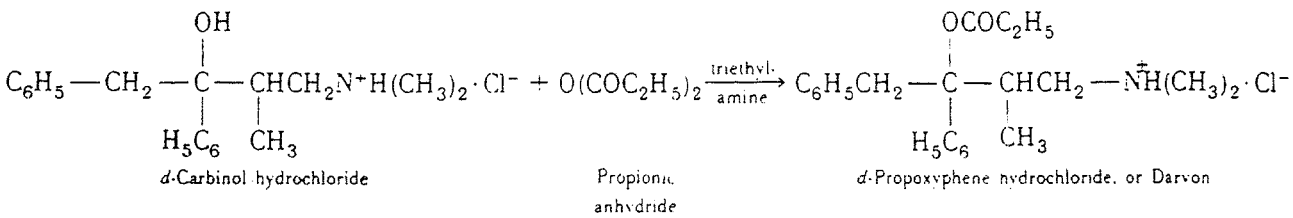
Step 2. Coupling Mannich ketone with benzyl chloride, using Grignard technique (and decomposition).



Step 3. Resolution of optical isomers by the use of *d*-camphorsulfonic acid in acetone.

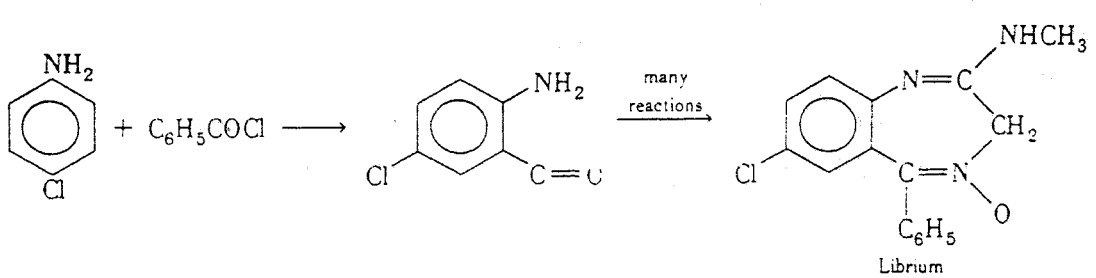
Step 4. Splitting off of the *d*-camphorsulfonic acid using ammonium hydroxide and conversion of the desired α-dextro isomer to the hydrochloride. Frequently, only one of the possible isomers of a compound has any therapeutic activity. In this case, only the dextro isomer is active as an analgesic.

Step 5. Esterification of the α-dextro isomer with propionic anhydride.



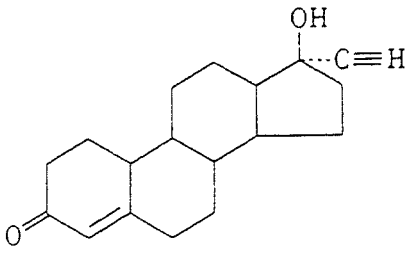
Step 6. Isolation, filtration, drying.

LIBRIUM. In 1976 Librium represented the second largest annual sale of a prescription medicinal. See Table 6.1. Librium (chlordiazepoxide hydrochloride) is made by a complex series of chemical conversions:

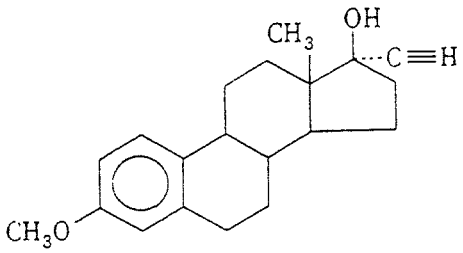


CONTRACEPTIVES. Oral contraceptives are taken daily by millions of women in the United States and throughout the world. Over 30 different products are marketed in the United States alone, in dosages that can be a combination of drugs, a sequence of drugs, or a single drug.

Most of the drugs in oral contraceptives are derived from the general formula:



For instance, one of the drugs, Mestranol, has the folmula:



RADIOISOTOPES IN MEDICINE[32]

Remington devotes chapter 29 to the use and medical applications of radioisotopes.

FERMENTATION AND LIFE PROCESSING FOR ANTIBIOTICS, BIOLOGICALS, HORMONES, AND VITAMINS

Historically the pharmaceutical industry has frequently used materials of plant or animal origin as sources of drugs. It was a logical step, although one a long time in coming, for this industry to employ the life processes of either plants or animals, and especially microorganisms, to produce useful medicaments. This is particularly true of fermentation, in which microorganisms are permitted to grow under controlled conditions to produce valuable and often complex chemicals. Some synthetic or semisynthetic processes can compete with life processes. Both life processes and a chemical synthesis are competitive in the production of riboflavin and chloramphenicol. Vitamin B_{12}[33] is produced by fermentation. See Chap. 4 for general principles of fermentation and for many products made biosynthetically.

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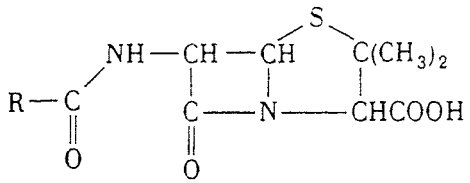
[32]RPS XVI, chap. 29, "Medical Applications of Radioisotopes," p. 458.

[33]Flowchart for Production of Vitamin B_{12} Feed Supplement, *Ind. Eng. Chem.* 46 240 (1954).

ANTIBIOTICS. The term antibiotic is a broad one, defined by Waksman[34] as "a substance produced by microorganisms, which has the capacity of inhibiting the growth and even of destroying other microorganisms by the action of very small amounts of the antibiotics." Approximately 3000 substances come under this classification,[35] but only about 70 have the necessary combination of patient safety, antimicrobial action, and stability. Penicillins, erythromycin, tetracycline, and cephalosporins are among the most widely used. See Table 6.2. Synthetic modifications of the naturally occurring antibiotic compounds have produced many variations that have clinically superior properties.

Although many antibiotics are now produced commercially, processes with flowcharts for the isolation of three representative ones are shown in Fig. 6.5. Antibiotics have presented many problems to the chemist, the microbiologist, and the chemical engineer since these compounds are often unstable to heat, wide pH ranges, and enzymatic action, and are often decomposed in solution.

PENICILLIN.[36] A number of penicillins, differing only in the composition of the R group, have been isolated from natural media, and hundreds have been semisynthesized. Penicillin G USP, with benzyl for R, generally the most clinically desirable, is the type commercially available, usually combined in salt form with procaine or potassium.



Not only was penicillin the first antibiotic to be produced for widespread use, but it is important in quantities made and in general usefulness. It is practically nontoxic and is one of the most active antimicrobial agents known. Hypersensitivity reactions occur in about 10% of patients. It is also useful in animal feeds to promote growth. It is a tribute to the pharmaceutical industry that the price of penicillin has been reduced from the initial price of $25,000 per gram to $35 per kilogram for procaine penicillin, with a production of over 2950 t in 1981.

It is possible to assist the synthesis of a desired penicillin by supplying the appropriate precursor[37] to the culture, i.e., the acid of the side chain which appears in the amide linkage with 6-aminopenicillanic acid in the final product. The mold preferentially incorporates the precursor added into the corresponding penicillin to the relative exclusion of other precursors present in or formed from the nutrient raw materials in the medium. Thus, to produce benzylpenicillin, the precursor phenylacetic acid is used. Several hundred modifications of the penicillin molecule not found in nature have been made by altering the side chain (R) by use

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[34]Waksman, An Institute of Microbiology: Its Aims and Purposes, *Science* **110** (27) 839, (1949).

[35]Buyske, Drugs from Nature, *CHEMTECH* 5 (6) 361 (1975).

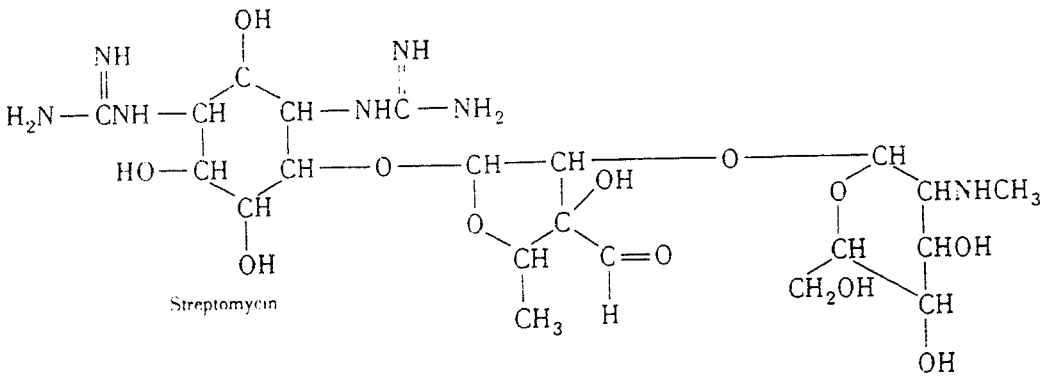
[36]RPS XVI, p. 1135; ECT, 3d ed., vol. 2, 1979, p. 809.

[37]A precursor is defined in the antibiotic industry as a chemical substance that can be incorporated into an antibiotic. The precursor may be used in such a way that an antibiotic modification not normally made by the organism is produced.

of the appropriate precursor in the fermentation.[38] An important modification is penicillin V (V-cillin K, Lilly, potassium phenoxymethyl penicillin), which is produced biosynthetically by using phenoxyacetic acid as a precursor (Fig. 6.5).

ERYTHROMYCIN. Erythromycin USP is, like penicillin, also isolated by solvent-extraction methods. It is an organic base, and extractable with amyl acetate or other organic solvents under basic conditions rather than the acidic ones which favor penicillin extraction.

STREPTOMYCIN.[39] The commercial method for producing this compound is also aerobic submerged fermentation, as outlined in Fig. 6.5 and the appended description. Its formula is



Streptomycin

The structure of streptomycin indicates its highly hydrophilic nature, and it cannot be extracted by normal solvent procedures. Because of the strong-base characteristics of the two substituted guanidine groups, it may be treated as a cation and removed from the filtered solution by ion-exchange techniques.

CEPHALOSPORINS.[40] Cephalosporins were marketed in the late 1950s when penicillin-fast organisms became prevalent. Later, chemically modified cephalosporins were developed to broaden the scope of their use and to be used where the originals were losing their effectiveness. At present, several third generation cephalosporins are awaiting Food and Drug Administration approval. Some of these are already on the market in Europe. Claims are made that these antibiotics are so broad in their activity that they can be used to treat patients before the infectious agent has been identified.

PRODUCTION AND ISOLATION OF PENICILLIN, ERYTHROMYCIN, AND STREPTOMYCIN. Figure 6.5 illustrates how these three important antibiotics of different chemical structure are formed by the life processes of three different microorganisms growing in individual pure cultures and how each one is extracted and purified. The steps in Fig. 6.5 may be

[38]Behrens et al., U.S. Patent 2,562,410 (1951).

[39]RPS XVI, p. 1127.

[40]Third-Generation Antiobiotics Join the Fray, *Chem. Week* 129 (8) 42 (1981).

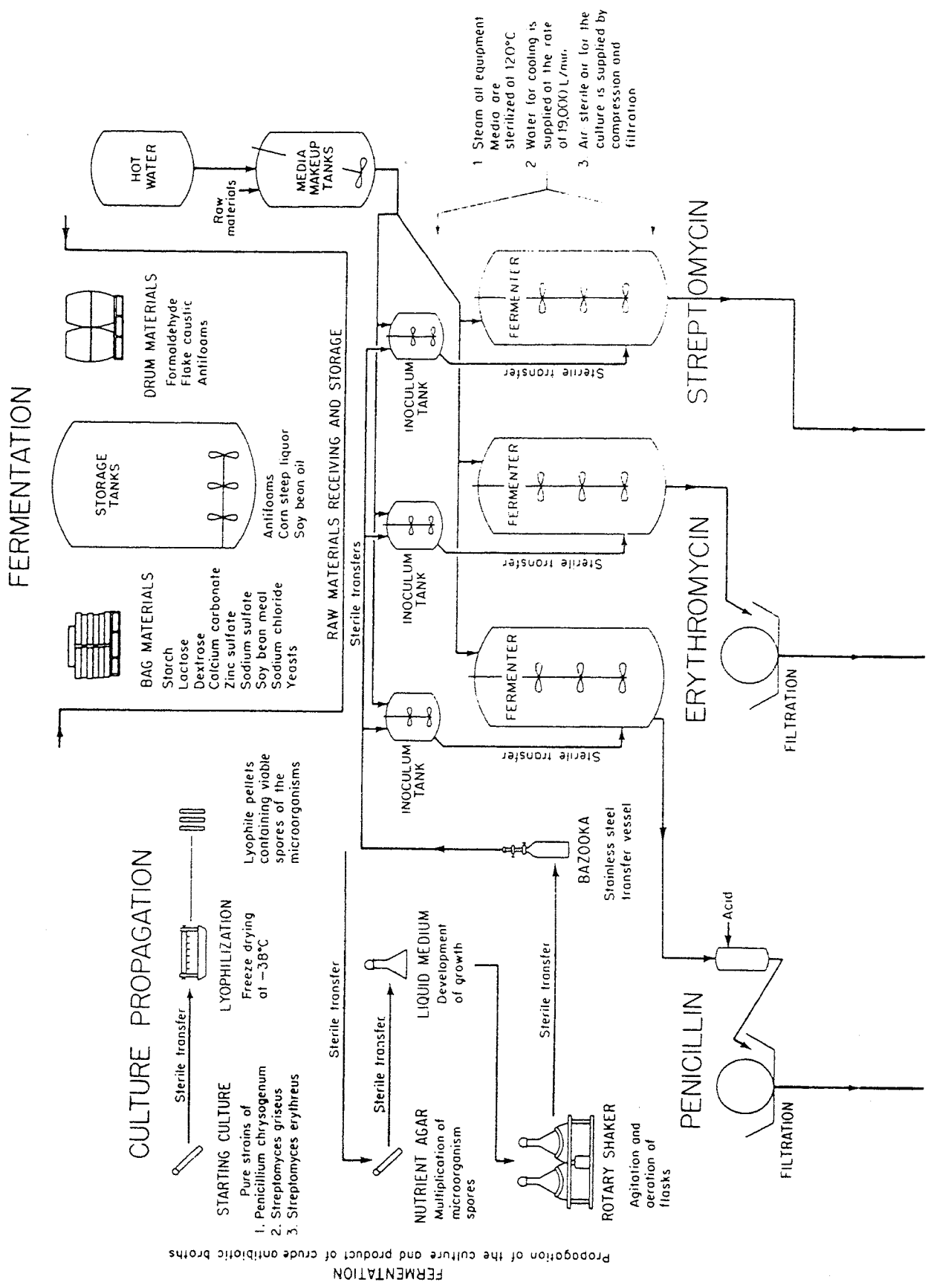
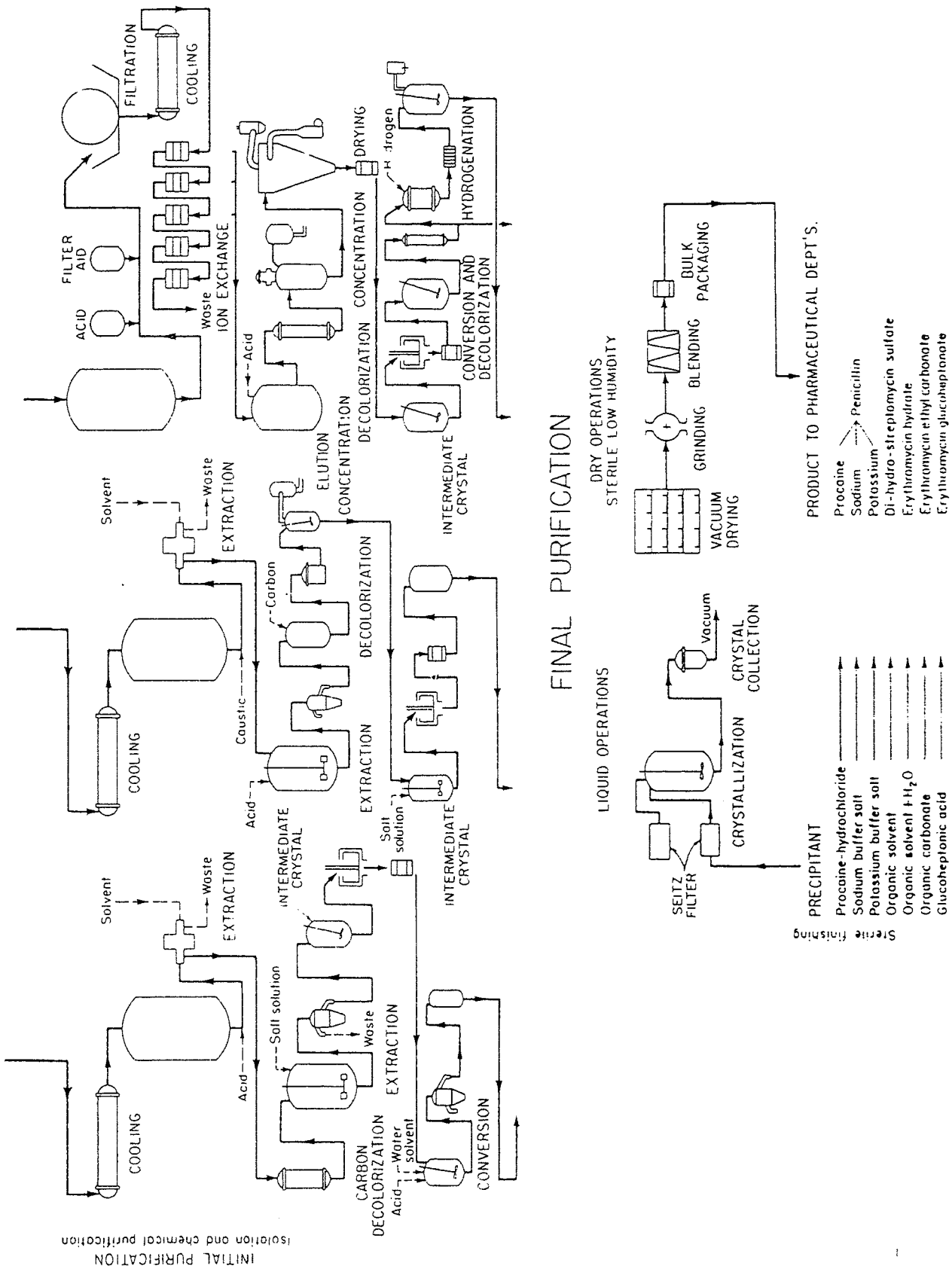


Fig. 6.5. Flowchart for the manufacture of antibiotics by fermentation, purification, extraction, and crystallization for penicillin and erythromycin, and with ion exchange for streptomycin. *(Eli Lilly & Co.)* Typical penicillin fermentation, approximate batch for 45,000-L fermenter (maintain pH preferably below 6.5 and not above 7 and temperature at 25 to 27°C):

Water	37,850 L	Precursor	500 kg
Sugar	3990 kg	Minerals	50 kg
Corn-steep liquor	500 kg	Time	100–150 h



For purification and isolation, 1800 kg of filter aid, 3785 L of amyl acetate, and 150 kg of procaine HCl are required. The yield of procaine benzylpenicillin (procaine penicillin G) is approximately 300 kg.

separated into the following coordinated sequences of *chemical conversions:*

Isolate and purify the required pure, active culture of the respective antibiotic from the starting culture on the slant through to the inoculum tank: for the culture of penicillin, *Penicillium chrysogesium;* of erythromycin, *Streptomyces erythreus;* of streptomycin, *Streptomyces griseus.*

Prepare and steam-sterilize at 120°C the fermentation media containing proteins, carbohydrates, lipids, and minerals.

Introduce the inoculum into the large, stirred, air-agitated fermenters to facilitate rapid metabolism. The air must be sterile.

Ferment, or "grow," the respective microorganism under conditions favorable to the planned antibiotic. Time, 100 to 150 h at 25 to 27°C.

Filter off the mycelium (cells and insoluble metabolic products) of the respective microorganism and wash, using a string discharge continuous rotary filter. Dry (sell for fertilizer).

The filtrates from the respective microorganism contain the antibiotic which must be *initially* purified and separated, and *finally* purified according to the properties of the respective antibiotic, as in the following outline.

For penicillin the purity is only 5 to 10%, impurities being medium components and metabolic products of the mold. Concentration is from 5 to 10 mg/ml.

Penicillin[41]

Cool the aqueous solution and acidify (H_2SO_4) to a pH of 2.0, resulting in an acid (and extractable) form of penicillin.

Solvent-extract in a Podbielniak countercurrent rotating contactor (Fig. 40.6) using a 1:10 volume of amyl acetate, giving a penicillin purity 75 to 80%.

Reverse the extraction at a pH of 7.5 into an aqueous solution with enhanced concentration and purity. Carbon-decolorize; add salt solution; quickly centrifuge to remove slime.

Stir to form intermediate crystal.

Centrifuge to recover intermediate crystal.

Recover values from the mother liquor by a countercurrent acidulated solvent (amyl acetate).

In the final purification, sterilize through Seitz filters.

Precipitate, e.g., with procaine HCl, to obtain procaine penicillin or as potassium or sodium salt.

Erythromycin[42]

Alkalize (NaOH) and solvent-extract (amyl acetate) in a Podbielniak countercurrent extractor.

Add acid and centrifugate the slime.

Decolorize with carbon.

Salt out the intermediate crystals and centrifuge.

Recrystalize or precipitate to obtain erythromycin.

Sterilize through Seitz filters.

Dry under sterile conditions.

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[41]Flowcharts for Penicillin, *Chem. Eng.* 64 (5) 247 (1957); Lowenheim and Moran, *Industrial Chemicals*, 4th ed., Wiley-Interscience, New York, 1975, p. 589.

[42]Hamel, *Antibiot. Chemother.* 11 328 (1961).

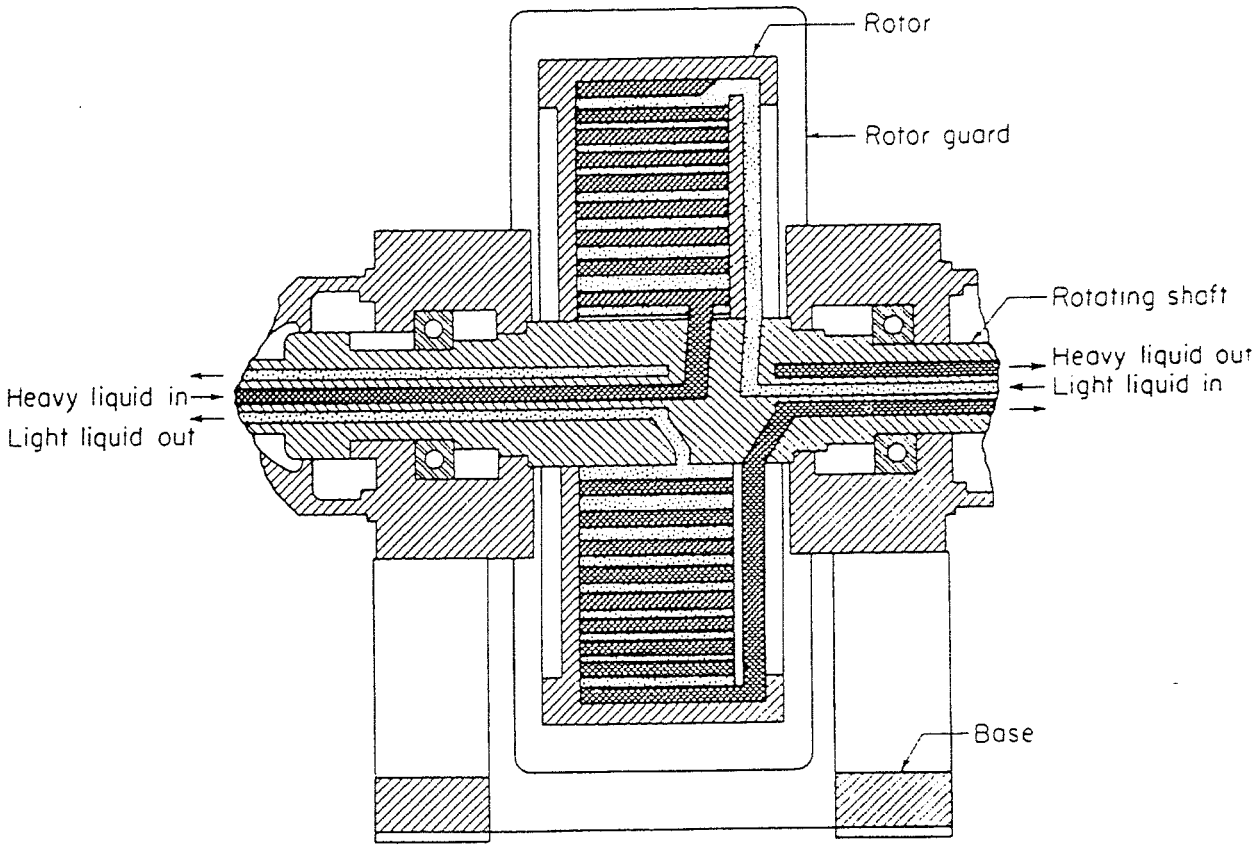


Fig. 6.6. The Podbielniak, or centrifugal, refiner, contactor, and separator. The liquids are introduced through the rotating shaft. The light liquid is led internally to the drum periphery and then out through the axis. The heavy liquid is led through the rotating shaft to the axis of the drum and out from the drum periphery. Rapid rotation causes a radial counterflow of the two liquids. [*See Perry, pp. 21-29; Todd and Podbielniak, Centrifugal Extraction, Chem. Eng. Prog.* 61 *(5) 69 (1965).*]

Streptomycin

Extract streptomycin from the aqueous "beer" with concentrations of 10 to 15 mg/ml by ion-exchange resin (Rohm & Haas IRC-50, carboxylic acid cation exchanger).

Elute from the resin with acidulated water.

Concentrate, decolorize, crystallize, and centrifuge the intermediate crystals.

Convert to desired salt and sterilize through a Seitz filter.

Dry under sterile conditions.

BIOLOGICALS

"Biologic product[43] means any virus, therapeutic serum, toxin, antitoxin, or analogous product applicable to the prevention, treatment, or cure of diseases or injuries to man." They arise from the action of microorganisms, and they are used for prophylaxis, treatment, and diagnosis of infections and allergic diseases. Their significance greatly increased with the introduction of Salk and Asian flu vaccines, followed by oral vaccines for poliomyelitis and the various types of measles vaccines. Biological products are valuable for producing immunity to infections and preventing epidemics of contagious diseases.

[43]RPS XVI, p. 1315 and chaps. 72–74 for further information.

STEROID HORMONES[44]

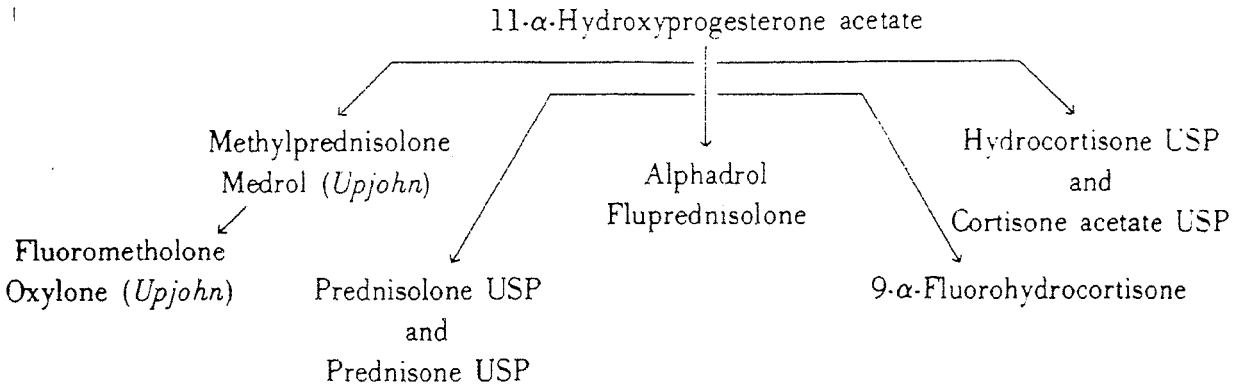
The annual value of bulk steroids produced in the United States increases continually. Steroids[45] used in medicine may be divided into the major classes of corticoids, anabolic androgens, progestational hormones, and estrogenic hormones. Most of those sold and used in medicine today are produced synthetically and are not naturally occurring steroids at all, but chemical modifications of them. There are, for example, at least 16 different so-called corticoids on the market (not counting their various esters and salts), only two of which—cortisone and hydrocortisone—are identical with those found in nature.

In medicine corticoids are perhaps more widely used than steroids of other types. They are used particularly in rheumatic diseases, in inflammatory conditions of the skin, and in allergic conditions. Other uses are in menstrual irregularities, menopause, and control of fertility and conception. There are many other indications for the use of steroids in medicine: in renal and cardiovascular diseases, in certain types of cancer, and in various types of stress reactions.

OUTLINE OF SYNTHESIS FROM SOYA, WHICH CONTAINS THE STEROID NUCLEUS:

$$\text{Crude soya sterols} \longrightarrow \text{stigmasterol} \xrightarrow[\text{steps}]{\text{chemical}^{46}} \text{progesterone}$$

Progesterone is converted[47] in high yield to the key intermediate for most of these sequences. 11-α-hydroxyprogesterone, by aerobic fermentation with a mold, such as *Rhizopus arrhizus*. Another fermentation step which enters into the synthesis of Medrol, Alphadrol, Oxylone, and other steroids, which have a double bond between C_1 and C_2, is dehydrogenation with a *Septomyxa* species. The following chart depicts briefly the various directions in which the key intermediate may be carried.



Other commercial processes for steroid hormone syntheses are based on bile acids and the plant steroid diosgenin obtained from a Mexican yam.

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[44]Courtesy of the Upjohn Co. See also RPS XVI, pp. 392, 902 ff.

[45]Applezweig, *Steroid Drugs*, vol. 1, McGraw-Hill, New York, 1962; vol. 2, Holden-Day, San Francisco, 1964.

[46]U.S. Patent 3,005,834; Lednicer and Mitscher, op. cit., p. 159.

[47]U.S. Patents 2,602,769; 2,735,800; 2,666,070.

VITAMINS

For *vitamins*, the U.S. Tariff Commission reports a total production of 19×10^3 t for 1981, with an average value of $19.88 per kilogram. Production methods by chemical synthesis are outlined in this chapter for ascorbic acid and riboflavin, and in Chap. 4 for riboflavin as a fermentation product. Remington[48] gives procedures for the manufacture and properties of the other vitamins.

ISOLATES FROM PLANTS OR ANIMALS

Although many important pharmaceutical products result from chemical engineering-directed life processes, fermentations, and syntheses, there are some important medicaments whose sole or competitive source is through isolation from plants and animals. Quinine is made by extraction from cinchona bark. Morphine and codeine are isolated from opium, theobromine from waste cacao shells, and caffeine from the decaffeinizing of coffee or from waste tea. Insulin is isolated from pancreas.

RESERPINE USP. Reserpine is one of the alkaloids widely employed for its tranquilizing effect upon the cardiovascular and central nervous systems and as an adjunct in psychotherapy. It is isolated by a nonaqueous solvent process, using, for example, boiling methanol extraction of the African root *Rauwolfia vomitoria*. Naturally, these extractions are carried out under countercurrent methods, details of which are in a flowchart published in *Chemical Engineering*.[49] The methanol extracts are concentrated and acidified with 15% acetic acid and then treated with petroleum naphtha to remove impurities. Extraction is made using ethylene dichloride. The solvent is neutralized with dilute sodium carbonate, evaporated to drive off the ethylene dichloride, and further evaporated to crystallize the crude reserpine crystals. These are further crystallized.

INSULIN INJECTION AND INSULIN ZINC SUSPENSION USP. Insulin, a hormone, plays a key role in catalyzing the processes by which glucose (carbohydrates) furnishes energy or is stored in the body as glycogen or fat. The absence of insulin not only interrupts these processes, but produces depression of essential functions and, in extreme cases, even death. Its isolation and purification were started in April 1922, by Lilly, following its discovery by Banting and Best.

The structure of insulin was elucidated by Sanger and others in 1945 to 1953[50]. Insulin is isolated from the pancreas of beef or hogs and was one of the first proteins to be obtained in crystalline form. In different concentrations and dissociations, the molecular weight of insulin varies between 36,000 and 12,000, and it has up to 51 amino acid units. Insulin protein is characterized by a high sulfur content in the form of cystine. It is unstable in alkaline solution. Insulin is isolated by extraction of minced pancreas with acidified alcohol, followed by purification, as presented in the flowchart in Fig. 40.7 and as outlined in the following description.

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[48]RPS XVI, pp. 945–978.

[49]*Chem. Eng.* 64 (4) 330–333 (1957); Colbert, *Prostagladin Isolation and Synthesis*, Noyes, Park Ridge, N.J., 1973.

[50]Sanger and Thompson, *Biochem. J.* 53 353 (1953).

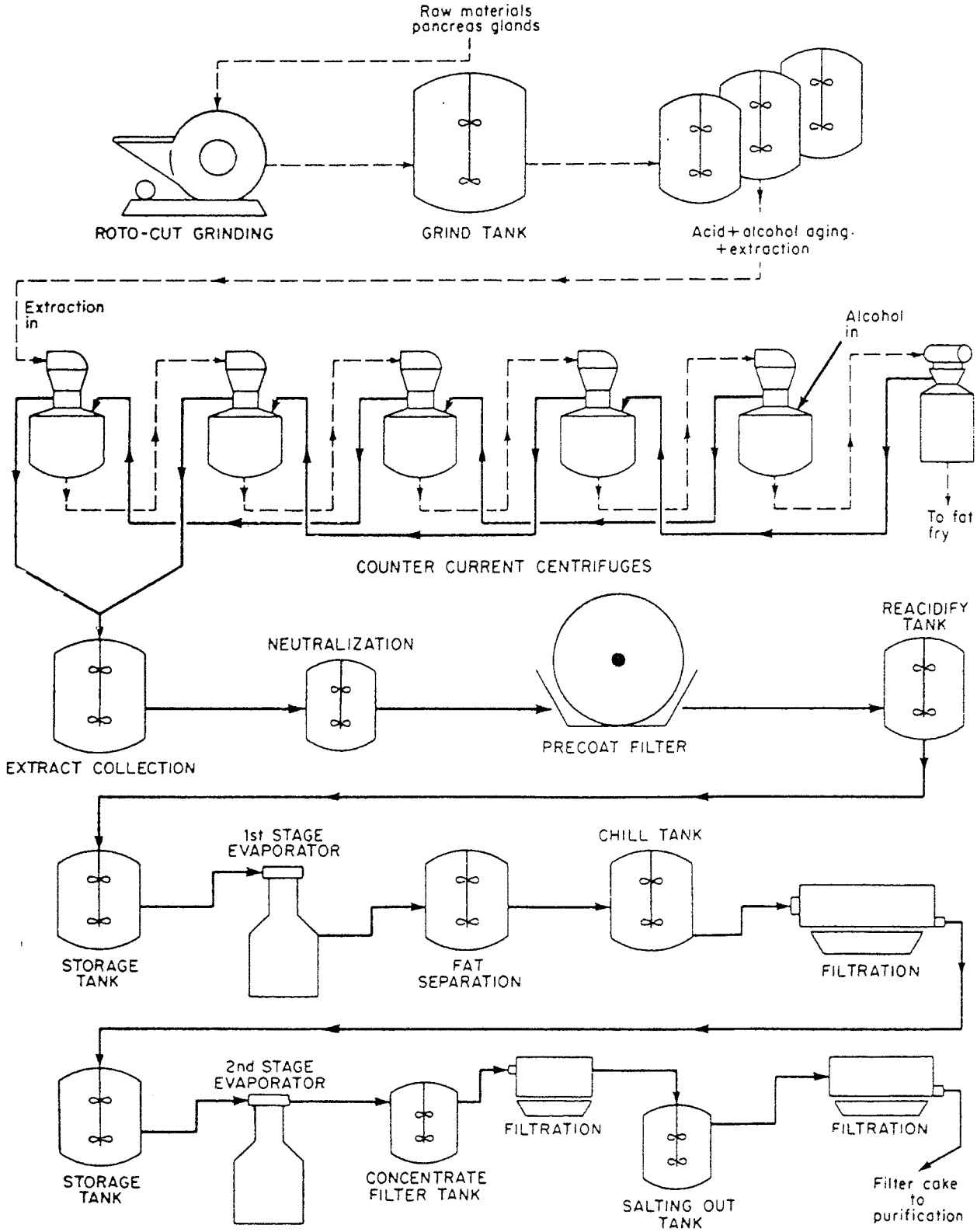

Fig. 6.7. The manufacture of insulin. *(Eli Lilly & Co.)*

Beef and pork pancreas glands are refrigerated at −20°C, rotoground, and the meat slurry is treated with ethyl alcohol after acidification.

With the use of continuous countercurrent extraction in, six continuous centrifuges over extraction tanks, the gland slurry is extracted with acidulated alcohol.

From the sixth centrifuge, the cake is processed in a hot-fat fry tank and discharged

through another centrifuge to separate waste fat from "fried residue," which is drummed and sold.

The crude alcoholic extract is run from two strong extraction-centrifuge units into a collection tank from which the extract is neutralized with ammonia and filter aid added.

In a continuous precoat drum filter, the cake is separated and washed, the clear liquor going to the reacidification tank.

In evaporators, the first stage removes alcohol, with subsequent waste-fat separation. The extract goes to a chill tank, with filter aid added, through a filter press and into the second evaporator.

From the second evaporator, the concentrated extract is filtered and conducted to the first salting-out tank, followed by filter-press filtration with filtrate to sewer and salt cake to purification for the second salting out. A filtration follows with filtrate to sewer.

The second-salting-out product is crystallized twice to furnish Iletin (insulin) crystals.

A method of preparing human insulin[51] is by gene splicing, or a recombinant DNA technique. Two strains of genetically modified bacteria are used to synthesize the two parts (chains A and B) of insulin. The chains are removed from the fermentation mixture and chemically joined together. Swine insulin is similar to human insulin except for a single amino acid building block. A Danish enzyme manufacturer claims to be able to modify swine insulin by replacing one amino acid thus converting it to human type. It is hoped that human insulin will not cause as many side effects in humans as the long-used swine insulin.

COCAINE HYDROCHLORIDE USP.[52] This alkaloid, isolated from *Erythroxylon coca*, formerly obtained from Peruvian coca leaves containing 0.5 to 1%, is now isolated mostly from Java coca leaves containing 1.5 to 2%. In the former, cocaine was the predominating alkaloid and was prepared without great difficulty. However, the Java leaves contain a mixture of cocaine and related alkaloids as the methyl esters of cinnamyl- and benzoyl-ecgonine. The cocaine and by-alkaloids are extracted commercially by alkalizing the ground leaves with a 10% sodium carbonate solution and percolating countercurrently in large steel percolators, using kerosene or toluene. The total alkaloids are extracted from the kerosene or toluene by a process which blows them up with a 5% sulfuric acid solution in tanks. The extracted kerosene or toluene is returned to the percolators. From the sulfuric acid solution, the mixed alkaloids are precipitated by alkalizing with sodium carbonate. The precipitated crude alkaloids are slowly boiled in an 8% sulfuric acid solution for several days to split all the alkaloids to ecgonine. During the splitting, many of the organic acids, like benzoic, are partly volatilized from the kettle with the steam. Those acids that are still suspended and those that crystallize out on cooling are filtered off. The acid aqueous solution of ecgonine is neutralized with potassium carbonate and evaporated. The low-solubility potassium sulfate is filtered hot. Upon cooling, the ecgonine crystallizes out. After drying, it is methylated, using methanol and 92% sulfuric acid, filtered, and washed with alcohol. The methylecgonine sulfate is benzoylated to cocaine in a very vigorous reaction with benzoyl chloride in the presence of anhydrous granular potassium carbonate. The cocaine is extracted from the potassium salts with ether and removed from the ether by sulfuric acid extraction, precipitated with alkali, and crystallized from alcohol. To form the hydrochloride, an alcoholic solution is neutralized with "acid alcohol"

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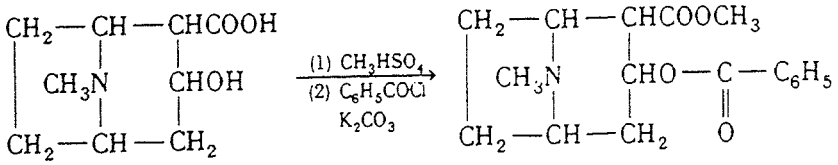
[51]Lilly's Insulin Has a Rival, *Chem. Week* 127 (11) 22 (1980).

[52]RPS XVI, p. 999; ECT, 3d ed., vol. 1, 1979, p. 891; Ashley, *Cocaine, Its History, Uses and Effects*, St. Martins Press, New York, 1975.

(HCl dissolved in absolute C_2H_5OH), and the cocaine HCl crystallized. The synthetic reactions are



Ecgonine $C_9H_{15}NO_3$

Cocaine $C_9H_{13}NO_3(CH_3)\cdot(COC_6H_5)$

In recent years, because of decreased demand, cocaine is obtained as a by-product in the preparation of a decocained extract of *Erythroxylon coca*, this being one of the principal flavors of Coca-Cola and other cola beverages. The procedure is to alkalize the *Erythroxylon coca* and extract *all* the alkaloids with toluene. The decocainized leaf is dried and extracted with sherry wine to give the flavoring extract.

MORPHINE SULFATE USP AND CODEINE PHOSPHATE USP. Remington says that "morphine is one of the most important drugs in the physician's armamentarium, and few would care to practice medicine without it, analgesia being one of the main actions. Codeine is now used to a larger extent than morphine and, while its analgesic action is only one-sixth of morphine, it is employed for its obtunding effect on the excitability of the cough reflex."[53] Morphine (about 11%) and codeine (about 1%) are extracted, along with many of the other alkaloids occurring in opium, by mixing sliced opium balls or crushed dried opium with lime water and removing the alkaloidal contents by countercurrent aqueous techniques. Other solvents are also used, for instance, acetone and acetic acid or acidulated water. The crude morphine alkaloid is precipitated with ammonium chloride, purified by crystallization of one of its inorganic salts from water, and centrifuged; such a crystallization is repeated if necessary. The purified sulfate or hydrochloride is converted into the alkaloid by ammonia precipitation. If a still further purified alkaloid is needed, it can be prepared by crystallization from alcohol. Otherwise the morphine alkaloid is dissolved in water with sulfuric acid and crystallized in large cakes from which the mother liquor is drained and then sucked off. The sulfate is dried and cut into convenient sizes for the manufacturing pharmacist to compound it, make it into tablets, or otherwise facilitate its use by the physicians.

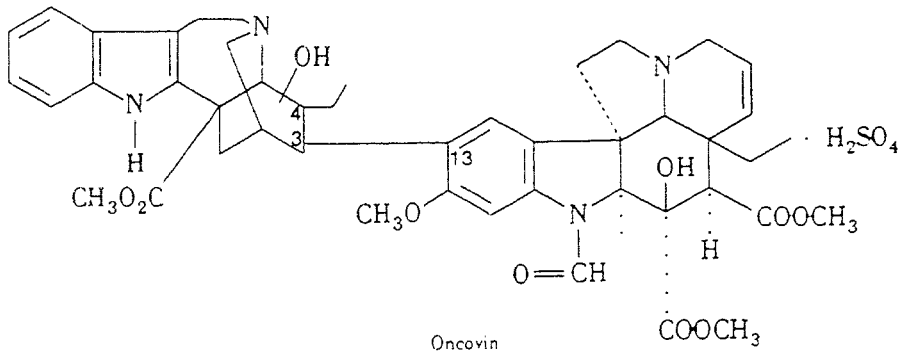
The *codeine* that occurs naturally in the opium is isolated from the aqueous morphine alkaloidal mother liquors by immiscible extraction with a nonaqueous solvent. Dilute sulfuric acid is employed to extract the codeine sulfate from the nonaqueous solvent. This solution is evaporated, crystallized and recrystallized. The alkaloid is precipitated from a sulfate solution by alkali and purified, if necessary, by alcoholic crystallization. It is converted into the phosphate by solution in phosphoric acid, evaporation, crystallization, centrifugation, and drying.

CAFFEINE USP. See caffeine under Alkylation for synthetic production. Much caffeine has been isolated from waste tea, and in recent decades, from the decaffeinization of coffee. The latter process involves extraction at 70°C of the moistened whole coffee bean with an organic solvent, frequently trichloroethylene, reducing the caffeine to about 0.03 from 1.2%. Rotating countercurrent drums are employed. The solvent is drained off, and the beans steamed to remove residual solvent. The beans are dried, roasted, packed, and sold. The extraction sol-

[53]Bentley, *Chemistry of the Morphine Alkaloids*, Oxford Univ. Press, New York, 1954; Small and Lutz, *Chemistry of the Opium Alkaloids*, U.S. Govt. Printing Office, 1932.

vent is evaporated, and the caffeine is hot-water-extracted from the wax, decolorized with carbon, and recrystallized.

VINCA ROSEA ALKALOIDS.[54] An alkaloid derived from *Vinca rosea* Linn has been the basis of two products: *Velban* (vinblastine sulfate, $C_{46}H_{58}N_4O_9 \cdot H_2SO_4$), useful in choriocarcinoma and Hodgkin's disease, and *Oncovin* (vincristine sulfate, $C_{46}H_{54}N_4O_{10} \cdot H_2SO_4$), indicated for acute leukemia in children. It takes 13.5 t tons of periwinkle leaves and 15 weeks of precision chemical processing involving chromatography to yield a single ounce of one of these drugs. Oncovin is probably represented by the formula



Oncovin

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[54]Sittig, op. cit., p. 645.

MINISTRY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF

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CHEMICAL TECHNOLOGY II

B.Tech (Second Year)

Chemical Engineering

PART 1

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Chapter 1

Phosphorus Industries

The use of artificial fertilizers, phosphoric acid, and phosphate salts and derivatives has increased greatly, chiefly because of aggressive and intelligent consumption promotion on the part of various manufacturers and federal agencies. However, before full consumption of these products could be achieved, more efficient and less expensive methods of production had to be developed. During recent decades, the various phosphate industries have made rapid strides in cutting the costs both of production and distribution and have thus enabled phosphorus, phosphoric acid, and its salts to be employed in wider fields and newer derivatives to be introduced. Supplementing the development of more efficient phosphorus industries have been the pure chemical studies of phosphorus, in its old and in its new compounds. These phosphates are not simple inorganic chemicals, as was assumed several decades ago, and their study has become a unique and complicated branch of chemistry that may some day be compared with the carbon (organic) or silicon branches of today. The properties of phosphorus chemicals are unique because of the important role of phosphorus in many biochemical processes, the ability of polyphosphates to complex or sequester many metal cations, and versatility in forming various types of organic and inorganic polymers.

HISTORICAL. The use of phosphatic materials as fertilizers was practiced unknowingly long before the isolation and discovery of phosphorus by the German alchemist Brand in 1669. As early as 200 B.C., the Carthaginians recommended and employed bird droppings to increase the yields from their fields. The Incas of Peru prized guano and bird droppings on their islands so highly that it was made a capital offense to kill birds. We are also familiar with the use of fish and bones by American Indians in their crude agricultural methods. Bones and guano continued to be the chief sources of phosphorus and phosphoric acid until after the middle of the nineteenth century, but these supplies were and still are limited. In 1842, a British patent was issued to John B. Lawes for the treatment of bone ash with sulfuric acid. This patent marked the beginning of a large acid phosphate industry which became the basis of our domestic fertilizer industry. Soon afterward various grades of phosphate ores were discovered in England. These were first finely ground and applied directly to the soil. It was soon recognized, however, that treatment of these phosphate minerals with sulfuric acid increased the availability and efficiency of the phosphate for agricultural purposes. At present, acidulation with nitric acid or strong phosphoric acid gives enhanced fertilizer values.

PHOSPHATE ROCK

USES AND ECONOMICS. See Table 1.1. The most important use of phosphate rock is in fertilizers. See Chap. 26 on Agrichemical Industries. Table 1.2 is a compilation of phosphate-rock treatment processes. Tricalcium phosphate in raw and/or steamed and degreased bones and in basic slag is also used after grinding as a direct phosphate fertilizer. A small percentage of the former is sometimes treated with sulfuric acid for superphosphate or as a source material for phosphate chemicals. Large tonnages of phosphate rock are converted to phosphorus or phosphoric acid and their derivatives.

Domestic phosphate rocks are essentially fluorapatite admixed with various proportions of other compounds of calcium, fluorine, iron, aluminum, and silicon.

The formula of fluorapatite is $CaF_2 \cdot 3Ca_3(PO_4)_2$, equivalent to $Ca_{10}F_2(PO_4)_6$. This compound is extremely insoluble. The various means for making the P_2O_5 content more soluble, not necessarily in water, but in plant juices (as measured by "citrate solubility"), are manufacture of various superphosphates and the defluorination of fluorapatite by calcination at incipient fusion temperatures of 1400 to 1500°C with silica or phosphoric acid.

The production of phosphate rock is concentrated in Florida with 87 percent of the total; the western states of Idaho, Montana, and Utah contribute 10 percent, and Tennessee 3 percent. In 1980, 54×10^6 t with a value of $1200 million were produced.[1] Table 16.3 shows the various uses of the rock.

[1] t = 1000 kg.

Table 1.1 Phosphate Rock Statistics (thousand metric tons and thousand dollars unless otherwise specified)

	1977	1978	1979	1980	1981
United States					
Mine production	166,893	173,429	185,757	209,883	183,733
Marketable production	47,256	50,037	51,611	54,415	53,624
Value	$821,657	$928,820	$1,045,655	$1,256,947	$1,437,986
Average per metric ton	$17.39	$18.56	$20.26	$23.10	$26.82
Sold or used by producers	47,437	48,774	53,063	54,581	45,526
Value	$829,084	$901,378	$1,063,517	$1,243,297	$1,212,433
Average per metric ton	$17.48	$18.48	$20.04	$22.78	$26.63
Exports[a]	13,230	12,870	14,358	14,276	10,395
P_2O_5 content	4,251	4,118	4,611	4,554	3,300
Value	$288,603	$297,357	$356,481	$431,419	$373,192
Average per metric ton	$21.81	$23.10	$24.83	$30.22	$35.90
Imports for consumption[b]	158	908	886	486	13
Customs value	$6,079	$24,379	$21,595	$12,856	$420
Average per metric ton	$38.47	$26.85	$24.37	$26.45	$32.31
Consumption[c]	34,365	36,812	39,591	40,791	35,144
World:					
Production	[d]119,310	[d]128,620	[d]132,913	[e]138,333	[f]138,630

[a]Exports reported to the Bureau of Mines by companies.

[b]Bureau of the Census data.

[c]Measured by sold or used plus imports minus exports.

[d]Estimated. [e]Preliminary. [f]Revised.

SOURCE: *Minerals Yearbook 1981*, U.S. Dept. of Interior, 1982, p. 649.

***Table* 1.2** Phosphate-Rock Processing, Products, and By-Products

Process	Raw Materials and Reagents	Main Products and Derivatives	By-products
Acidulation	Phosphate rock, sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, ammonia, potassium chloride	Superphosphate, phosphoric acid (wet process), triple superphosphate, monoammonium phosphate, diammonium phosphate, monopotassium phosphate	Fluorine compounds, vanadium, uranium (limited)
Electric-furnace reduction	Phosphate rock, siliceous flux, coke (for reduction), electrical energy, condensing water	Phosphorus, phosphoric acid, triple superphosphate, various Na, K, NH_4, Ca salts; phosphorus pentoxide and halides	Fluorine compounds, carbon monoxide, slag (for railroad ballast aggregate, fillers, etc.), ferrophosphorus, vanadium*
Calcium metaphosphate	Phosphate rock, phosphorus, air or oxygen, fuel	Calcium metaphosphate	Fluorine compounds
Calcination or defluorination	Phosphate rock, silica, water or steam, fuel	Defluorinated phosphate	Fluorine compounds

*Vanadium is present in appreciable quantities only in the western phosphates.

***Table* 1.3** Phosphate Rock Sold or Used by Producers in the United States, by Use (thousand metric tons)

Use	1980		1981	
	Rock	P_2O_5 Content	Rock	P_2O_5 Content
Domestic*				
Wet-process phosphoric acid	33,884	10,444	29,085	8,956
Normal superphosphate	333	107	184	60
Triple superphosphate	1,348	436	1,198	378
Defluorinated rock	430	145	492	166
Direct applications	37	8	27	6
Elemental phosphorus	4,083	1,067	4,055	1,049
Ferrophosphorus	190	49	89	22
Total†	40,305	12,256	35,131	10,638
Exports‡	14,276	4,554	10,395	3,300
Grand total†	54,581	16,810	45,526	13,939

*Includes rock converted to products and exported.

†Data may not add to totals shown because of independent rounding.

‡Exports reported to the Bureau of Mines by companies.

SOURCE: *Minerals Yearbook 1981*, U.S. Dept. of Interior, 1982, p. 654.

Phosphate rock, when very finely pulverized, has limited direct use as a fertilizer, chiefly because of the relatively slow availability of the P_2O_5. However, it is mainly used as a raw material for the manufacture of phosphoric acid, superphosphate, phosphorus, and phosphorus compounds.

PROCESSING.[1] In Florida, both hard and pebble rock phosphate are mined. Hard rock phosphate occurs as nodules and boulders in irregular pockets, but its exploitation is limited. The more extensive and cheaply mined pebble deposits occur with an average overburden of 6 m, and their phosphatic value is too low for economical processing. The pebble deposits themselves, called the *matrix*, are from 3 to 9 m thick. This matrix is composed of clay slimes, silica sand, and phosphate pebble. Pebble sizes range from 1 to 27 mm. The overburden is removed and dumped into a previously mined-out cut. Electrically operated draglines remove the matrix and drop it into an excavated area. Hydraulic guns break down the mud in the matrix and wash it into the pump suction, where it is transported through pipes by large sand pumps to the beneficiation plant (Fig. **1.1**).

In Tennessee four types of phosphate rock are found, nodular, blue, white, and brown. Only the latter is mined at present, using open-pit, dry methods. The overburden varies greatly and has an average depth of from 1.8 to 2.4 m. Although originally deposited in horizontal strata, in the large western fields layers of phosphate rock have been severely folded, faulted, and elevated by crustal deformations and resemble fissure veins. The rock may contain approximately 75% bone phosphate of lime[2] but, because of admixture with wall material, it usually averages nearer 70% BPL (Table **1.4**). Because of its rather soft structure, the rock has a moisture content of 4 to 6%. It is generally mined by underground methods. Western phosphate rock contains anywhere from 50 to 200 g of uranium per metric ton of rock. The complicated and costly recovery process now in use extracts uranium from phosphate rock via wet-process phosphoric acid, and the uranium goes into solution upon treatment with sulfuric acid. After filtration, the bulk of the uranium is found in the acid filtrate. Some is recovered, presumably by an ion-exchange technique. Fluorine and vanadium are also valuable by-products from phosphate rock.

In the Florida pebble district, initially only coarse phosphate rock was recovered, which had a high BPL, whereas the fines, with a much lower BPL, representing about equal tonnage, were wasted. In the 1920s, experimental work was started to develop a froth-flotation process which would increase the BPL of the fines or raw matrix to at least 66 or 68% from about 40% or less. This procedure is frequently spoken of as *beneficiation*, and one of the successful processes currently employed is illustrated in Fig. 16.1. Such upgrading operations are of far-reaching and increasing importance, as easily mined or better-grade deposits of phosphate rock, and other minerals, are becoming exhausted. These operations not only produce a higher grade of product, but allow larger amounts to be recovered, beneficiated, and used, even in the case of such a low-priced product as phosphate rock.

The matrix from the Florida phosphate pebble deposits is received at the beneficiation plant as a slurry. There it is washed to remove clays and fine particles. The +16 mesh pebble product is drained and sent to storage bins as a marketable product. The −16 mesh material is deslimed in hydrocyclones to remove the −150 mesh material, which is predominately

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[1]Slack (ed.), *Phosphoric Acid*, Dekker, 1968; ECT, 2d ed., Vol. 15, 1968, p. 232; Crerar, H_3PO_4 Route Cuts Costs, *Chem. Eng.* 80 (10) 62 (1973).

[2]This is usually abbreviated BPL and actually means tricalcium phosphate, the chief inorganic constituent of bones.

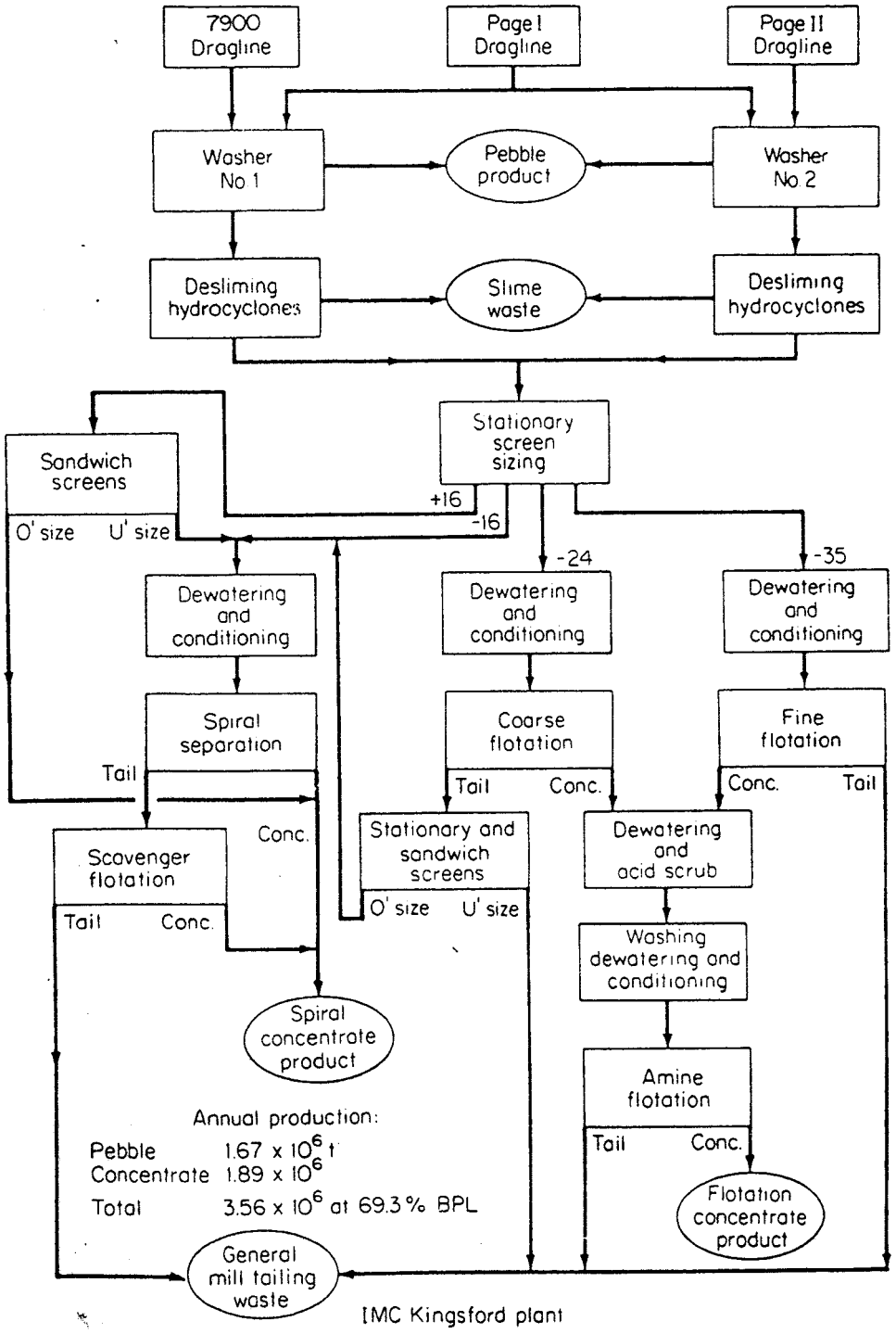


Fig. 1.1. Florida phosphate rock beneficiation flowsheet. *(International Minerals and Chemical Corp.)*

clays. The −16 to 150 mesh feed is sized on inclined stationary screens. The −16 to 24 mesh fraction is treated as shown in Fig. 16.1 to produce the spiral concentrate product. This is a skin flotation operation using Humphrey spirals.

The froth flotation circuit is separated into fine and coarse floats at 35 mesh because this allows for greater overall recovery of the coarser fractions. Flotation reagents such as saponified fatty acids (soap skimmings) are added. The coarse concentrates are further treated with another flotation step using an amine flotation agent. The final concentrate has a 72 to 78% BPL range.

***Table* 1.4** Phosphate Rock Sold or Used by Producers in the United States, by Grade and State in 1981 (thousand metric tons and thousand dollars)

Grade (% BPL* content)	Florida and North Carolina			Tennessee		
	Rock	P_2O_5 Content	Value	Rock	P_2O_5 Content	Value
Below 60	79	17	1,274	698	170	5,732
60 to 66	5,553	1,585	171,443	681	187	11,669
66 to 70	25,727	7,962	639,586	—	—	—
70 to 72	2,984	967	90,303	—	—	—
72 to 74	2,761	929	102,219	—	—	—
Plus 74	1,371	477	60,015	—	—	—
Total†	38,475	11,938	1,064,839	1379	357	17,401

	Western States			Total United States		
	Rock	P_2O_5 Content	Value	Rock	P_2O_5 Content	Value
Below 60	1783	445	16,999	2,560	632	24,005
60 to 66	907	250	14,243	7,140	2,022	197,354
66 to 70	1614	506	46,353	27,341	8,468	685,939
70 to 72	1368	443	52,599	4,353	1,410	142,902
72 to 74	—	—	—	2,761	929	102,219
Plus 74	—	—	—	1,371	477	60,015
Total†	5672	1644	130,194	45,526	13,939	1,212,433

*1.0% BPL (bone phosphate of lime or tricalcium phosphate) = 0.458% P_2O_5.

†Data may not add to totals shown because of independent rounding.

SOURCE: *Minerals Yearbook, 1981*, U.S. Dept. of Interior, 1982, p. 654.

The waste contains only a small percentage of phosphate ore and is run to a tailing area. Figure 1.2 shows a materials balance flowsheet for the mining and beneficiation of phosphate rock; on average about 4.7 t of product are made per work hour.

SLIME WASTE.[3] The slime wastes from the desliming hydrocyclones occupy about 32 times the initial volume of the rock because of the process water added to separate the matrix from the slime. This volume of waste material plus the tailings from the matrix concentration procedures are impounded by earthen dams. These impounded waste areas (often as large as 320 ha) serve to act as holding tanks to dewater the waste, as reservoirs to minimize water discharge from the mining area, to capture and hold rainwater, and to ultimately densify and store the waste clay. It requires many years to fulfill the design storage level of 25% solids inside the dam.

The phosphate industry currently disposes of 60 percent of these wastes below ground level and is reclaiming mined out land. The holding ponds are not environmentally esthetic and there has been a demand that all these wastes be disposed of below ground level. Because the volume of waste products from mining and beneficiation of phosphate rock exceeds the mined-out volume, this is extremely difficult. Over the past 20 years millions of dollars in

[3]Lawver, The Clay Waste Problem (private communication from International Minerals and Chemical Corp.).

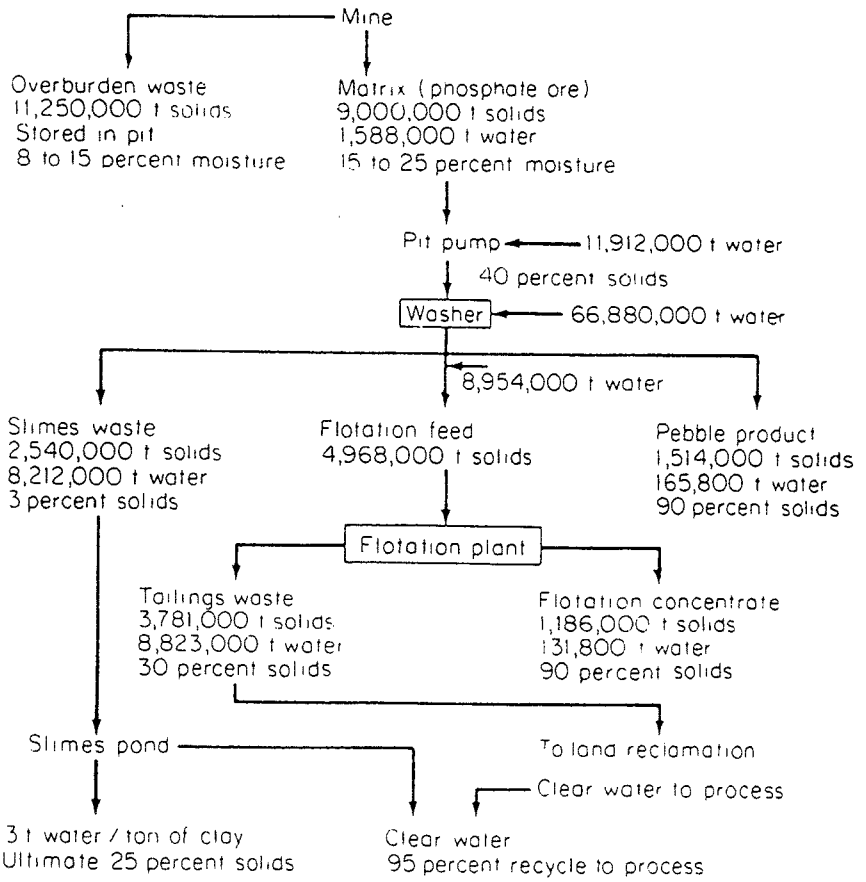


Fig. 1.2. Material balance flowsheet for Florida phosphate rock. Material flow in metric tons per year. *(International Minerals and Chemical Corp.)*

research have been spent in an effort to improve the current waste handling methods. To date no proven large-scale system has been developed that is better, either environmentally or economically.

SUPERPHOSPHATES[4]

The acidulation of phosphate rock to produce superphosphate has been the most important method of making phosphate available for fertilizer purposes for nearly a century. See Chap. 26 on agrichemicals. The reactions are

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow \underset{\text{Monocalcium phosphate}}{CaH_4(PO_4)_2} + 2\underset{\text{Gypsum}}{(CaSO_4 \cdot 2H_2O)}$$

$$CaF_2 + H_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2HF\uparrow$$

$$4HF + SiO_2 \rightarrow SiF_4\uparrow + 2H_2O$$

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$$

[4]ECT, 3d ed., vol. 10, pp. 71–76, 1980.

The following is a more probable expression of the main reaction:

$$\underset{\text{Phosphate rock or fluorapatite}}{CaF_2 \cdot 3Ca_3(PO_4)_2} + \underset{53\text{–}57°\text{Bé}}{7H_2SO_4} + 3H_2O \rightarrow \underset{\text{Monocalcium phosphate}}{3CaH_4(PO_4)_2 \cdot H_2O} + 2HF\uparrow + \underset{\text{Anhydrite}}{7CaSO_4}$$

The hydrofluoric acid reacts as shown above, forming fluosilicic acid, but with incomplete removal of fluorine. An excess of sulfuric acid is consumed by such impurities in the phosphate rock as $CaCO_3$, Fe_2O_3, Al_2O_3, and CaF_2. The product increases in weight over the 70 to 75 BPL phosphate rock used, as much as 70 percent resulting in a superphosphate with 16 to 20% available P_2O_5. The manufacture of superphosphate involves four steps: (1) preparation of phosphate rock, (2) mixing with acid, (3) curing and drying of the original slurry by completion of the reactions, and (4) excavation, milling, and bagging of the finished product. Although newer plants use continuous processes, some plants still conduct these operations stepwise. All plants first pulverize the rock. With modern pulverizing and air-separation equipment, most rock is ground to an average fineness of 70 to 80 percent through a 200-mesh screen, with the following benefits: (1) the reaction rate is faster; (2) more efficient use is made of the sulfuric acid and consequently less acid is needed; and (3) a higher grade of product in better condition is obtained.

NORMAL SUPERPHOSPHATE.[5] The continuous process is depicted by Fig. 1.3, where ground phosphate rock (90 percent minus 100 mesh) is fed by a weigh feeder into a double-conical mixer (TVA), where it is thoroughly mixed with metered quantities of sulfuric acid. The sulfuric acid is diluted with water in the cone to a concentration of 51°Bé, the heat of dilution serves to heat the sulfuric acid to proper reaction temperature, and excess heat is dissipated by evaporation of extra water added. The rate of water addition and acid concentration may be varied to control product moisture. The acid and water are fed into the cone mixer tangentially to provide the necessary mixing with the phosphate rock. The fresh superphosphate drops onto the den conveyor, which has a very low travel speed to allow about 1 h for solidifying before reaching the disintegrator. The disintegrator slices the solid mass of crude product so that it may be conveyed to pile storage for "curing," or completion of the chemical reaction, which takes 4 to 6 weeks to reach a P_2O_5 availability acceptable for plant food. The continuous den is enclosed so that fumes do not escape into the working area. These fumes are scrubbed with water sprays to remove acid and fluoride before being exhausted to the atmosphere. The scrubber water is discharged to a limestone bed to neutralize the acid.

Nitric and mixed acid acidulation of phosphate rock.[6] Europe probably first used nitric and mixed acid acidulation of phosphate rock. The substitution of nitric for sulfuric acid is desirable, since nitrogen has an essential value as plant food and can be resold at its purchase price. Simple acidulation of phosphate rock with nitric acid produces a hygroscopic superphosphate, since it contains calcium nitrate. The TVA and others have studied and recommended commercial processes. In one, the phosphate rock is extracted by mixed nitric and

[5]Young and Davis, *The Role of Phosphorus in Agriculture*, chap. 7, ASA-CSSA-SSSA, Madison, Wisc., 1980.

[6]Davis, Meline and Graham, TVA Mixed Acid Nitric Phosphate Process, *Chem. Eng. Prog.*, **64** (5) 75 (1968); Jorquera, Nitric vs. Sulfuric Acidulation of Phosphatic Rock, *Chem. Eng. Prog.*, 64 (5) 83 (1968).

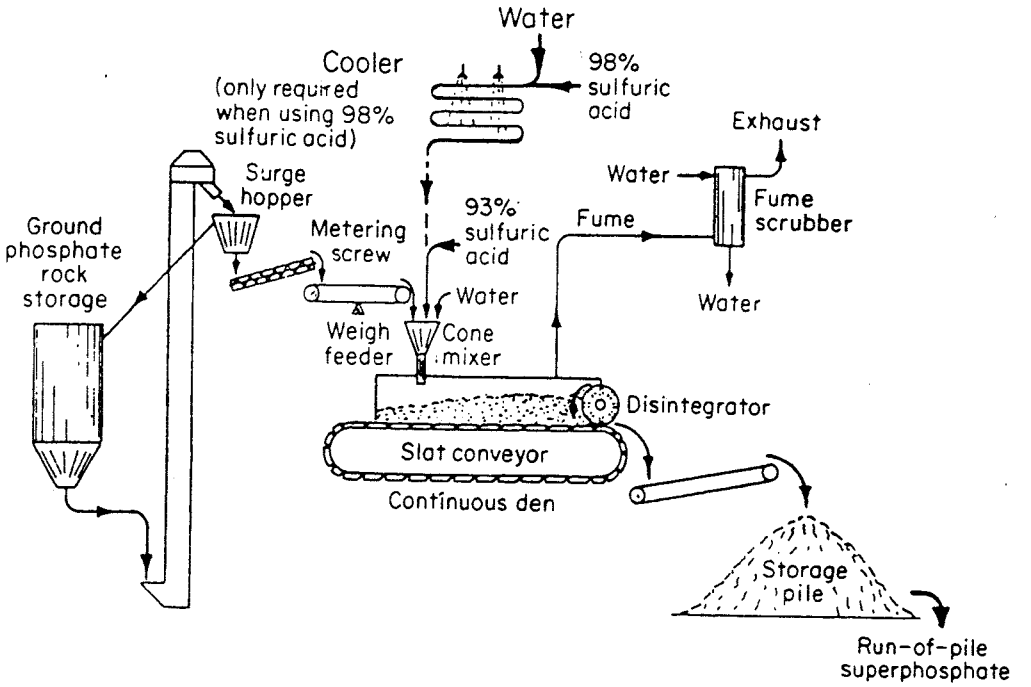


Fig. 1.3. Flowchart for the manufacture of superphosphate. *(Tennessee Valley Authority.)*

sulfuric acids, followed by ammoniation, drying, and the addition of potassium chloride (optional). Another features mixed nitric and phosphoric acidulation, followed by the conventional steps, and others use nitric acid alone for acidulation. These processes, as well as conditioning against moisture absorption as practiced for ammonium nitrate, have led to an extension of the acidulation with nitric acid. Nitrophosphate is also gaining in Europe. Phosphate rock is decomposed with nitric acid plus a small amount of phosphoric acid. The resulting slurry is ammoniated and carbonated and, if desired, combined with potassium salts and spray-dried to yield a uniform pelletized product.

TRIPLE SUPERPHOSPHATE. This material is a much more concentrated fertilizer than ordinary superphosphate, containing from 45 to 46% of available P_2O_5, or nearly three times the amount in regular superphosphate. Triple superphosphate is made by the action of phosphoric acid on phosphate rock; no diluent calcium sulfate is formed.

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF\uparrow$$

The TVA continuous granular triple superphosphate production process is illust
Fig. 1.4. Pulverized phosphate rock is mixed with phosphoric acid in a two-st
The resultant slurry is sprayed into the granulator. The granulator contain
from the process. The product from the granulator is dried, screened,
and cooled again. The final product is conveyed to bulk storage whe
4 to 6 weeks during which time a further reaction of acid and roc
the availability of P_2O_5 as plant food. The exhaust gases from the g
scrubbed with water to remove silicofluorides.

Nongranular superphosphate is also available and is prepared using a cone-mixe
veyor belt similar to that used to prepare normal (ordinary) superphosphate. As the
is only 14 to 20 min as compared with 40 to 50 min for normal superphosphate, a si
cupped conveyor belt can be used instead of the slat-type den.

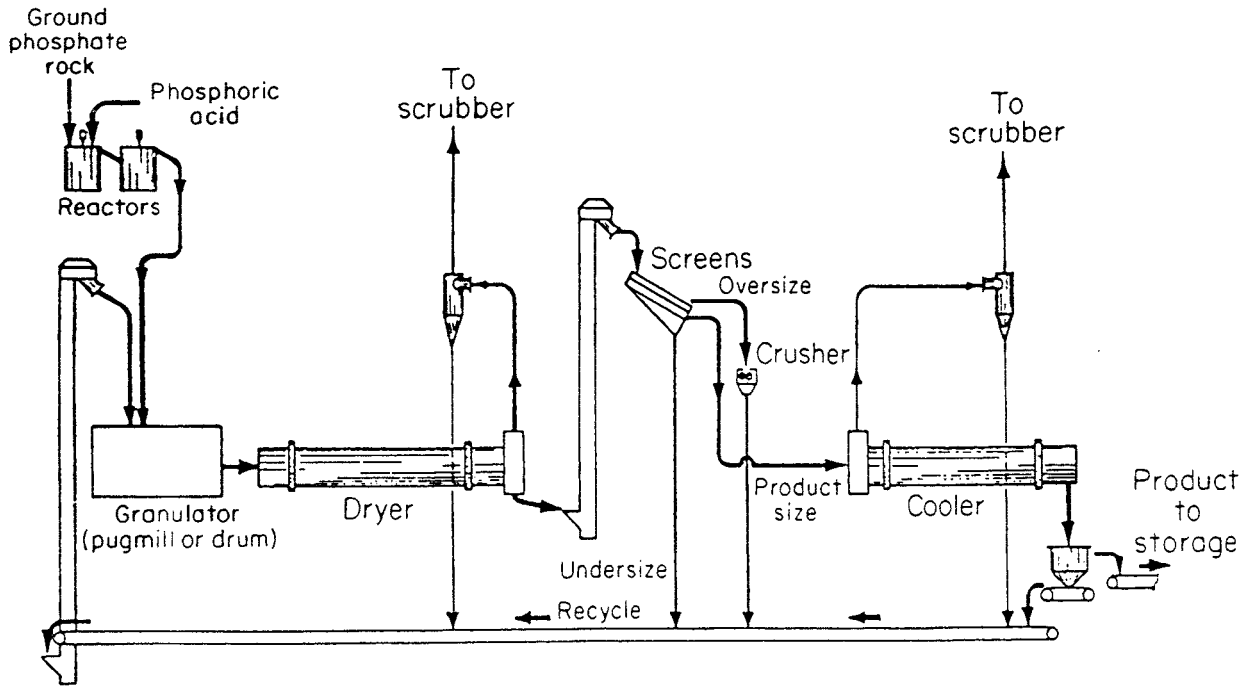


Fig. 1.4. Flowchart illustrating a triple superphosphate process. *(Tennessee Valley Authority.)*

WET-PROCESS PHOSPHORIC ACID

USES AND ECONOMICS. Rapid expansion in the manufacture of wet-process phosphoric acid has resulted from the increased demand for high-analysis fertilizer, triple superphosphate, and ammonium and dicalcium phosphates.

Much earlier, most of the orthophosphoric acid produced was prepared by the action of dilute sulfuric acid, 50°Bé, on ground phosphate rock or bones. This method was supplanted by the Dorr[7] strong-acid process, which produced a strong and economical acid. The equipment must be lined with lead, stainless steel, Hastelloy G, or acid-proof brick, and sufficient time provided in the various agitators for the reaction to go to completion. The temperature in the digester must be kept low enough to ensure the precipitation of gypsum ($CaSO_4 \cdot 2H_2O$), and not anhydrite. If the latter is formed, it subsequently hydrates and causes plugging of pipes. Acid made by this process is used almost entirely in fertilizer production, where impurities are unimportant, or after some purification for various sodium phosphates. Pure acid is obtained from elemental phosphorus by the electric-furnace process.

New methods are being developed to purify wet-process acid by solvent extraction using a mixture of di-isopropyl ether and tributyl phosphate as solvent.[8] This process produces pure enough acid to be used for pharmaceuticals and cattle feed.

The major end uses of phosphoric acid are fertilizer, 85 percent; detergent materials, 5 percent; animal feed, 5 percent; and food, beverages, and dentifrices, 5 percent. Excluding fertilizers, the main outlet for phosphorus derivatives has been in soap and detergent manufacture as various sodium phosphates. Because of their ability to precipitate or sequester lime and magnesia, to emulsify or disperse solids in the detergent solution, and to augment the

[7]See CPI 2, p. 353 for flowchart.

[8]Davister and Peterbroeck, The Prayon Process For Wet Acid Purification, *Chem. Eng. Prog.* 78 (3) 35 (1982).

inherent detergent properties of soap and synthetic surfactive agents, these salts have been much used as *soap builders* or *detergent synergists*. Recent concerns about water pollution and algae growth due to the phosphorus content of wastewater have greatly decreased the amount of phosphates in detergents

P_2O_5 production in 1982 was a little over 9×10^6 t of which 8.5×10^6 t was wet-process acid and the remainder "furnace" acid.[9] Exports accounted for almost 10^6 t.

MANUFACTURE. The chief process[10] for producing wet-process phosphoric acid is by the use of sulfuric acid as shown in Figs. 16.5 and 16.6. The essential reactions are:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 2HF\uparrow + 6H_3PO_4$$

or, more simply expressed,

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + \underset{\text{Gypsum}}{3CaSO_4 \cdot 2H_2O}$$

Raw phosphate rock, or occasionally calcined rock if a clear, green acid is desired, is digested with sulfuric acid. The retention time ranges from 1.5 to 12 h, and conditions are controlled to produce gypsum crystals that are readily filterable. The reaction is cooled using a vacuum (flash) cooler. The reaction mixture is filtered using a Bird-Prayon tilting-pan filter shown in Fig. 1.6. This process produces 28 to 32% acid which then must be concentrated for most uses.

[9]Key Chemicals, Phosphoric Acid, *Chem. Eng. News*, 60 (4) 20 (1982).

[10]Fertilizer Needs Spur Wet-Process Phosphoric, *Chem. Eng. News* 45 (12) 54 (1967).

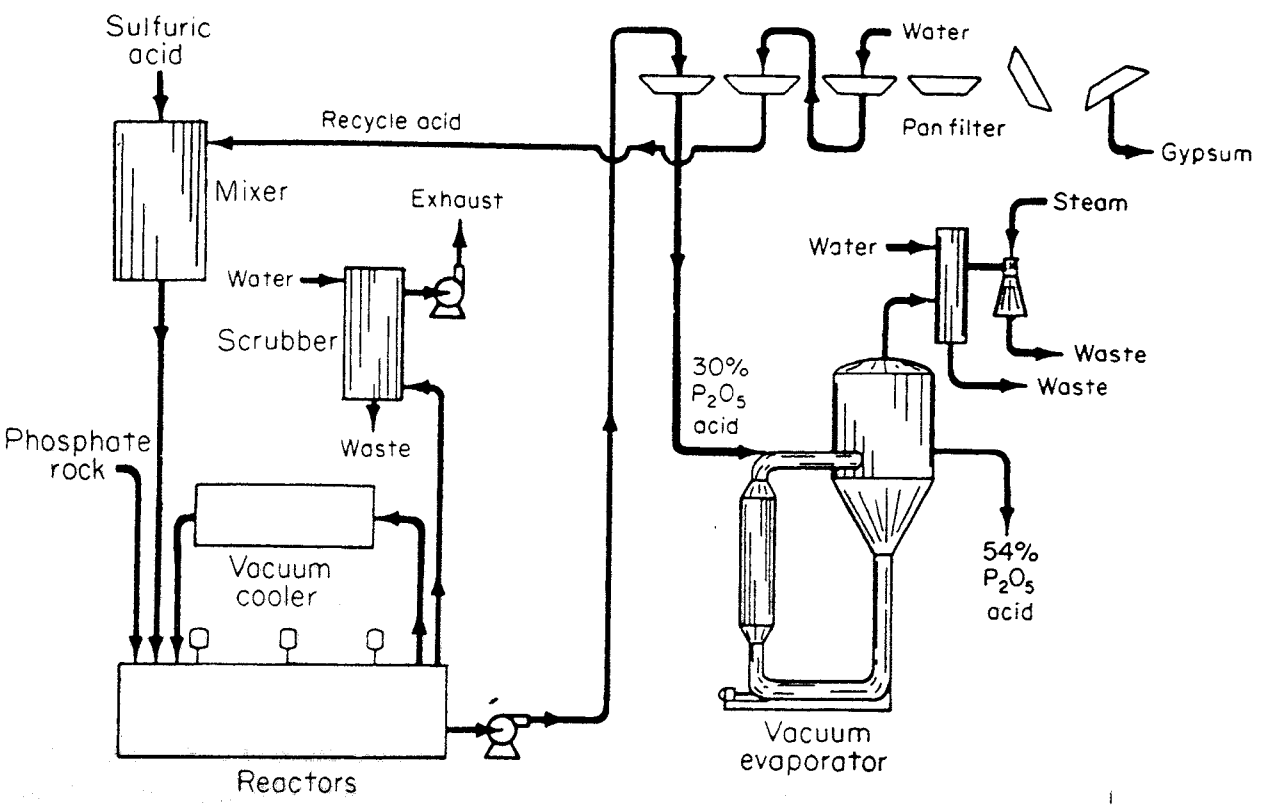


Fig. 1.5. Wet-process phosphoric acid manufacture, using Bird-Prayon tilting-pan washing filters. The overall efficiency is 94 to 98 percent producing an acid of 30 to 32% P_2O_5 concentration.

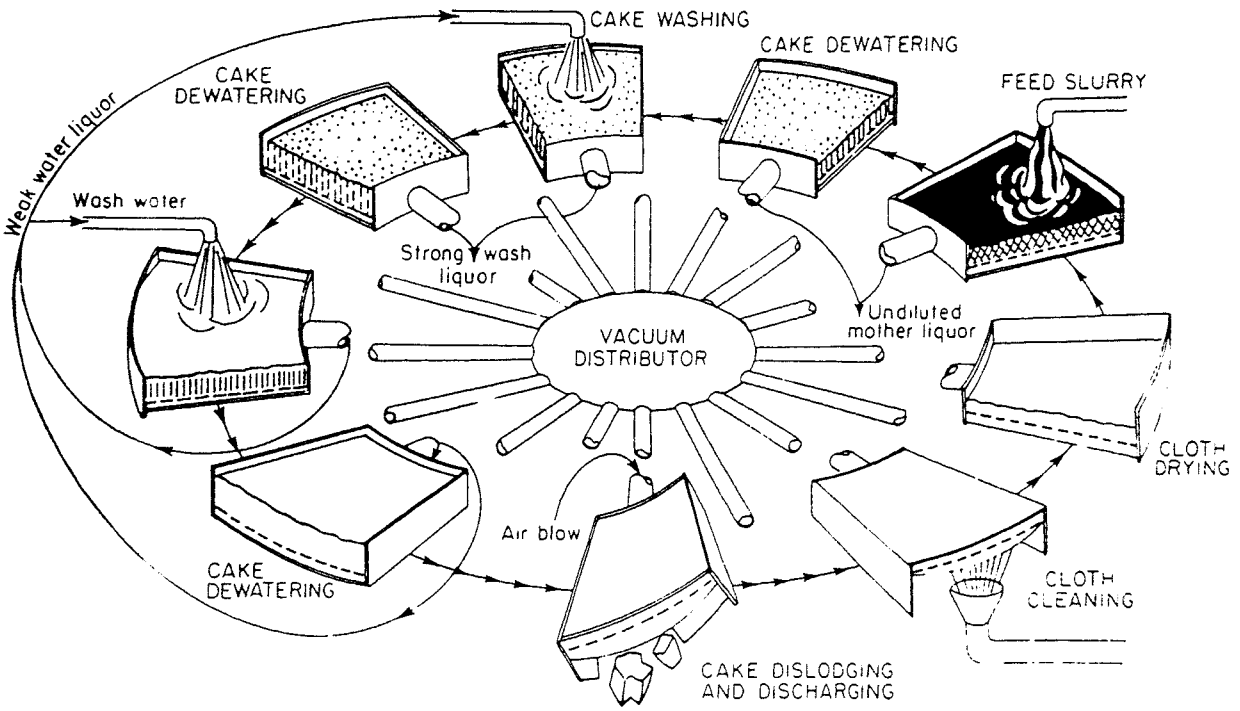


Fig. 1.6. The Bird-Prayon tilting-pan filter for phosphoric acid manufacture. The feed continuously enters the pans, which are connected to the vacuum source. The circular frame supporting the pans rotates so that each pan is moved successively under the desired number of washes. After the final wash liquor has completely drained off, the vacuum is released and the pan is inverted a full 180°. The cake drops off, its removal being ensured by a reverse blast of air through the filter medium, which is then scoured fresh and clean by a high-pressure shower while the pan is still inverted. The filter-medium and drainage area are then purged by vacuum, and the pan returned to the feed position. *(Bird Machine Co.)*

Another process is the Swenson isothermal phosphoric acid reactor which uses a single vessel vacuum crystallizer. The advantages claimed for this process are: reduced capital cost, utilities consumption, and maintenance costs and high operating efficiency with improved P_2O_5 recovery.[11] Recently the idea of producing the calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) instead of the usual dihydrate has been tried.[12] Its disadvantage is that the hemihydrate is unstable and could freeze in the pipes, but the big advantage is that it produces 42 to 50% acid directly without a costly evaporation step as is necessary when the dihydrate is produced. Merchant grade acid is 54%.

Almost all U.S. producers are using the dihydrate process. In 1981 there was only one producer using the hemihydrate process, but as energy costs continue to rise it is expected that more plants will use the hemihydrate process. The potential energy saving is 2.3 to 3.5 GJ/t.

The Haifa process is another method of producing wet-process acid. It uses (1) hydrochloric acid to acidulate (in slight excess to prevent formation of monocalcium phosphate); (2) an organic solvent (C_3 or C_4 alcohols) to extract the phosphoric acid; (3) water to strip out the phosphoric acid (with a small amount of solvent and hydrochloric acid); concentration to

[11]Olivier, Wet Process Acid Production, *Chem. Eng. Prog.* 74 (11) 55 (1978); ECT, 3d ed., vol. 17, 1982, pp. 426–539.

[12]An Energy Saving Route to Phosphoric Acid, *Chem Week* 128 (2) 46 (1981); Davis, Cogeneration's Place in a Modern Facility, *Chem. Eng. Prog.* 78 (3) 46 (1982); Parkinson, Phosphoric Acid Process Proven for Large-Capacity Plants, *Chem. Eng.* 89 (18) 66 (1982).

remove the small amounts of solvent and hydrochloric acid and to yield a high-grade product. This process was developed in Israel and has been applied in Japan and the United States.[13] The recent dramatic increase in the price of sulfur (from $70 to $140 per metric ton between 1979 and 1981) has renewed interest in the nitric acid process, both for phosphoric acid and superphosphate.

PURIFICATION.[14] Crude wet-process acid is often black and contains dissolved metals and fluorine, and dissolved and colloidal organic compounds. Suspended solid impurities are usually removed by settling. Solvent extraction or solvent precipitation is used to remove the dissolved impurities. Solvent extraction uses a partially miscible solvent, such as *n*-butanol, isobutanol, or *n*-heptanol. The phosphoric acid is extracted, and the impurities are left behind. Back-extraction with water recovers the purified phosphoric acid. Solvent precipitation uses a completely miscible solvent plus alkalis or ammonia to precipitate the impurities as phosphate salts. After filtration, the solvent is separated by distillation and recycled

URANIUM RECOVERY.[15] Uranium is present in all U.S. phosphate rocks. Florida rock contains the most, and rock from western states contains the least. It is present as a trace constituent, but because of its high value, it is becoming important to recover it. The methods usually used are solvent extraction of wet-process acid with octyl pyrophosphoric acid (OPPA) in kerosene, extraction with a mixture of tri-N-octyl phosphine oxide and di-2-ethyl-hexyl phosphoric acid (TOPO-D_2EHPA) or use of TOPO-D_2EHPA combined with octylphenyl phosphoric acid (OPAP). The energy value of the uranium extracted, which is converted to yellow cake, U_3O_8, is ten times greater than the energy required to produce it. This could make the phosphate industry a net producer of energy.

In 1981 1.8×10^6 kg of yellow cake was recovered in the United States. This constituted about 10 to 15 percent of the U.S. demand. More than half the demand is potentially recoverable as a result of phosphoric acid production.

ELECTRIC-FURNACE PHOSPHORUS AND PHOSPHORIC ACID

This element was first produced on a small commercial scale by treating calcined bone with sulfuric acid, filtering off the phosphoric acid, and evaporating it to sp gr 1.45. This was mixed with charcoal or coke, again heated, the water evaporated off, then calcined at white heat in retorts. The phosphorus was thus distilled off, collected under water, and purified by redistillation. The production of phosphorus today still depends on volatilization of the element from its compounds under reducing conditions. During the past decades, the method has

[13]ECT, 3d ed., vol. 10, 1980, p. 69.

[14]McCullough, Phosphoric Acid Purification, *Chem. Eng.* 83 (26) 101 (1976); Bergdorf and Fischer, Extractive Phosphoric Acid Purification, *Chem. Eng. Prog.* 74 (11) 41 (1978); Davister and Peeterbroeck, The Prayon Process For Wet-Acid Purification, *Chem. Eng. Prog.* 78 (3) 35 (1982).

[15]Kouloheris, Uranium from Phosphoric Acid, *Chem. Eng.* 87 (16) 82 (1980); Berry, Recovery of Uranium from Phosphoric Acid, *Chem. Eng. Prog.* 77 (2) 76 (1981). Both articles have excellent flow sheets.

changed chiefly in details and size of production. Elementary phosphorus is manufactured on a large scale as a heavy chemical and shipped in tank cars from the point of initial manufacture, where raw materials are cheap, to distant plants for conversion to phosphoric acid, phosphates, and other compounds.

REACTIONS. Phosphorus is produced by the electric-furnace method (Fig. 1.7). The following reaction is considered to take place, the raw materials being phosphate rock, silica, and coke:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 9SiO_2 + 15C \rightarrow CaF_2 + 6P + 15CO$$

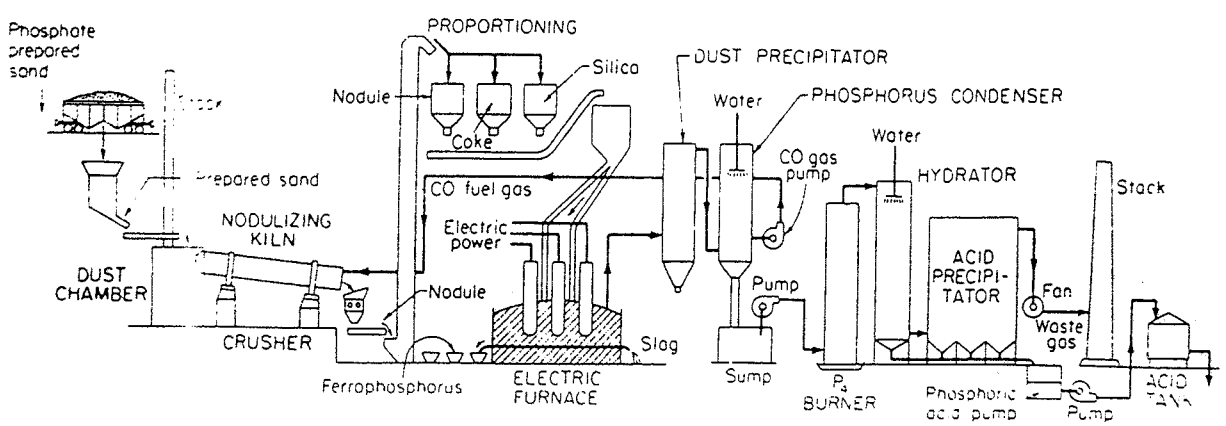
or, more simply expressed,

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4 + 10CO \qquad \Delta H = -3055 \text{ kJ}$$

The silica is an essential raw material which serves as an acid and a flux. About 20 percent of the fluorine present in the phosphate rock is converted to SiF_4 and volatilized. In the presence of water vapor this reacts to give SiO_2 and H_2SiF_6:

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

The fluorine is not recovered by manufacturers of phosphorus, but the CO is employed as a fuel in preparing the furnace charge. The slag tapped from the furnace is sold as ballast, or aggregate or fill. Ferrophosphorus is tapped as necessary, its quantity being dependent on the amount of iron originally in the burden or added to it. The phosphorus is employed usually as an intermediate product, being shipped to consumption centers and there burned or oxi-



In order to produce 1 t of 85% H_3PO_4, the following materials and utilities are needed:

Phosphate rock (35.6% P_2O_5)	1000 kg	Iron	(depends on ferrophosphorus requirements)
Silica rock	320 kg	Electricity	13,840 MJ
Coke	377 kg	Direct labor (est.)	0.5–1 work-h

Fig. 1.7. Phosphorus production flowchart. In most cases, the hot phosphorus is pumped into an insulated tank car and shipped to the oxidizing plant where it is made into phosphoric acid and various phosphates.

dized to P_2O_5, which is dissolved in water to form acids or other compounds:

$$\text{Phosphorus pentoxide: } 4P + 5O_2 \rightarrow 2P_2O_5 \qquad \Delta H = -3015 \text{ kJ}$$
$$\text{Orthophosphoric acid: } P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \qquad \Delta H = -188 \text{ kJ}$$

The foregoing reactions for ordinary or orthophosphoric acid are commercialized in the following sequences as exemplified by Figs. 1.5 and 1.6 for wet-process acid in comparison with Fig. 1.7 for phosphorus and furnace acid made therefrom.

Wet-Process Phosphoric Acid	Electric-Furnace Phosphorus and Acid
Phosphate rock is finely ground and prepulped in the mixing tank with cooled recycled H_3PO_4 from the slurry cooler.	Phosphate rock ground and sized.
Overflow from the mix tank is reacted with H_2SO_4 and recycled H_3PO_4 in an agitated digester system, forming gypsum crystals and H_3PO_4.	Rock and sand mixed with coke, sintered, and introduced into electric furnace.
Bulk of slurry is recycled through slurry cooler.	Mix heated and reduced at an elevated temperature.
Rest of slurry is conducted through the filter feed tank to the cells of the rotary Bird-Prayon tilting-pan filtration unit.	Slag and ferrophosphorus run off separately.
In the progressive and tilting pans of this filter, the H_3PO_4 is separated from the gypsum, using three-stage countercurrent washing.	Phosphorus vapor and CO drawn off, phosphorus condensed.
Gypsum is automatically dumped.	Phosphorus transported in tank cars to consuming centers.
Off-gases are scrubbed to remove fluorine before venting.	Phosphorus melted and sprayed into stainless-steel oxidation tower.
H_3PO_4 can be used directly (28–32% P_2O_5) or concentrated	Phosphorus oxidized to P_2O_5.
	P_2O_5 cooled and hydrated in stainless-steel hydrator or tower against water or dilute H_3PO_4.
	H_3PO_4 mist-precipitated in electrostatic precipitator or a Brink Mist Eliminator.
	H_3PO_4 filtered and purified.

The electric-furnace[16] process was first employed commercially in 1920. This process permits the use of lower-grade rock than the wet-process phosphoric acid process, since the slag carries off impurities. Indeed, lower grades are frequently preferred because of the better CaO/SiO_2 balance for slag formation. The principal requirement is cheap electricity.

The phosphate rock must be charged in lump form or as +8-mesh (Fig. 1.1). Fine material tends to block the exit of the phosphorous vapors and to cause bridging and uneven descent of the furnace charge, resulting in puffs and the carrying over of excessive quantities of dust. Phosphate lumps may be prepared in the following ways: (1) pelletizing by tumbling or extrusion, (2) agglomeration by nodulizing at high temperatures, (3) sintering a mixture of phosphate fines and coke, and (4) briqueting, with the addition of a suitable binder. After agglomeration, coke breeze and siliceous flux (gravel) are added, and the materials are charged to the electric furnace. Iron slugs are added to the charge if more ferrophosphorus is desired. A flowchart with the quantities required is shown in Fig. 16.7. The bottom of the furnace is composed of carbon blocks, and this lining extends up the wall to a point well

[16]Curtis, The Manufacture of Phosphoric Acid by the Electric Furnace Method, *Trans. AIChE* **31** 278 (1935); Mantell, *Electrochemical Engineering*, 4th ed., McGraw-Hill, New York, 1960, pp. 523–532 (data and diagram); Highett and Striplin, Elemental Phosphorus in Fertilizer Manufacture, *Chem. Eng. Prog.* 63 (5) 85 (1967); Bryant, Holloway and Silber, Phosphorus Plant Design, *Ind. Eng. Chem.* 62 (4) 8 (1970).

above the slag pool. From this point, a high-grade firebrick lining is used. A domelike steel top with a cast refractory lining caps the furnace. Openings for the electrodes and for introducing raw materials are included here. The electrodes are threaded so as to facilitate replacement as the carbon is consumed. The gases and phosphorus vapor are removed at one end of the furnace. The calcium-rich slag from the furnace is usually tapped periodically and crushed for use in the manufacture of glass, for the liming of soil, and as a roadbed ballast. The ferrophosphorus is tapped separately, or it runs out with the slag when it is separated and sold as a phosphorus additive for steel. In this process 80 percent of the fluorine stays with the slag. The small portion that leaves with the gas is absorbed in the water used in condensing the phosphorus.

Pure, strong phosphoric acid is manufactured from elemental phosphorus by oxidation and hydration. See Fig. 1.7 and preceding reactions and sequences for manufacture. The oxidation tower, or chamber, is constructed of acid-resistant brick or stainless steel.[17] Phosphoric acid runs down the walls and absorbs about 75 percent of the P_2O_5 and also heat. This acid is *cooled*, some drawn off, and some recirculated. The remaining 25 percent is passed as a mist to a Cottrell or Brink mist eliminator for collection. Some modern plants produce superphosphoric acid, 76% P_2O_5, equivalent to 105% orthophosphoric acid, with which higher-percentage plant foods can be made, e.g., ammonium polyphosphate, 54% superphosphate, and 10-34-0 liquid fertilizer. Other processing plants produce 75 to 85% orthophosphoric acid, depending on the process for which it is to be used.

Phosphoric acid of high P_2O_5 content consists of mixtures of various phosphates with a certain distribution of chain lengths. Individual molecular species are difficult to prepare. Pyrophosphoric acid ($H_4P_2O_7$) can be obtained only through a slow crystallization process, and above its melting point it rapidly reverts to a distribution of various chain phosphates. If P_2O_5 is carefully dissolved in cool water, most of the phosphate will be in the form of tetrametaphosphate rings.

PHOSPHATES

SODIUM PHOSPHATES. The various sodium phosphates represent the largest tonnage of chemicals based on pure phosphoric acid obtained mostly from elemental phosphorus. Phosphates are phosphorus compounds in which the anions have each atom of phosphorus surrounded by four oxygen atoms placed at the corners of a tetrahedron. Chains, rings, and branched polymers result from the sharing of oxygen atoms by tetrahedra. *Orthophosphates* are based on the simple PO_4 tetrahedron as a monomeric unit and include monosodium phosphate (MSP) (NaH_2PO_4); disodium phosphate (DSP) (Na_2HPO_4); and trisodium phosphate (TSP) ($Na_3PO_4 \cdot \frac{1}{4}NaOH \cdot 12H_2O$). The first two sodium salts are made from phosphoric acid and soda ash reacted in the proper molecular proportions; the solution is purified if necessary, evaporated, dried, and milled. TSP is also made from phosphoric acid and soda ash, but caustic soda is necessary to substitute the third hydrogen of the phosphoric acid. These salts are employed in water treatment, baking powder (MSP), fireproofing, detergents, cleaners, and photography (TSP). *Condensed or molecularly dehydrated* phosphoric acids and salts

[17]Brink, New Fiber Mist Eliminator, *Chem. Eng.* 66 183 (1959); Brink, in chap. 15B, *Gas Purification Processes for Air Pollution Control*, Nonhebel (ed.), Newnes-Butterworths, London, 1972; see Perry, pp. 18-82 to 18-93, for mist collection equipment.

have a H_2O/P_2O_5 molar ratio of less than 3 and greater than 1 and have the single chain unit P-O-P. The best known are the *polyphosphates:* pyrophosphates ($M_4P_2O_7$) and tripolyphosphates ($M_5P_3O_{10}$). When any of the condensed phosphoric acids are dissolved in water, hydrolysis to orthophosphoric acid takes place. Their salts are represented by the widely used sodium tripolyphosphate and tetrasodium and tetrapotassium pyrophosphates.

To produce sodium tripolyphosphate (Fig. 1.8), a definite temperature control is necessary. When MSP and DSP in correct proportions, or equivalent mixtures of other phosphates, are heated for a substantial time between 300 and 500°C and slowly cooled, the product is practically all in the form of the tripolyphosphate.

Figure 16.8 depicts the following coordinated sequences commercializing the reaction:

$$NaH_2PO_4 + 2Na_2HPO_4 \rightarrow Na_5P_3O_{10} + 2H_2O$$

Soda ash and ±75% phosphoric acid are reacted in the mix tank.

The orthophosphates are dried either in a rotary or spray dryer.

The sodium tripolyphosphate is molecularly dehydrated in a gas-fired calciner.

The tripolyphosphate is annealed, chilled, and stabilized in a continuous rotary tempering unit.

The product is milled, stored, and bagged.

Certain equipment modifications have been used, such as addition of an adjustment mixer following the reactor mix tank and a spray tower for drying of the orthophosphate, together with a long, continuous rotary to carry out the dehydrating (calcining), annealing, stabilizing, and cooling in one unit.

PYROPHOSPHATES. Tetrasodium pyrophosphate (TSPP) ($Na_4P_2O_7$), is used as a water softener and as a soap and detergent builder. It is manufactured by reacting phosphoric acid and

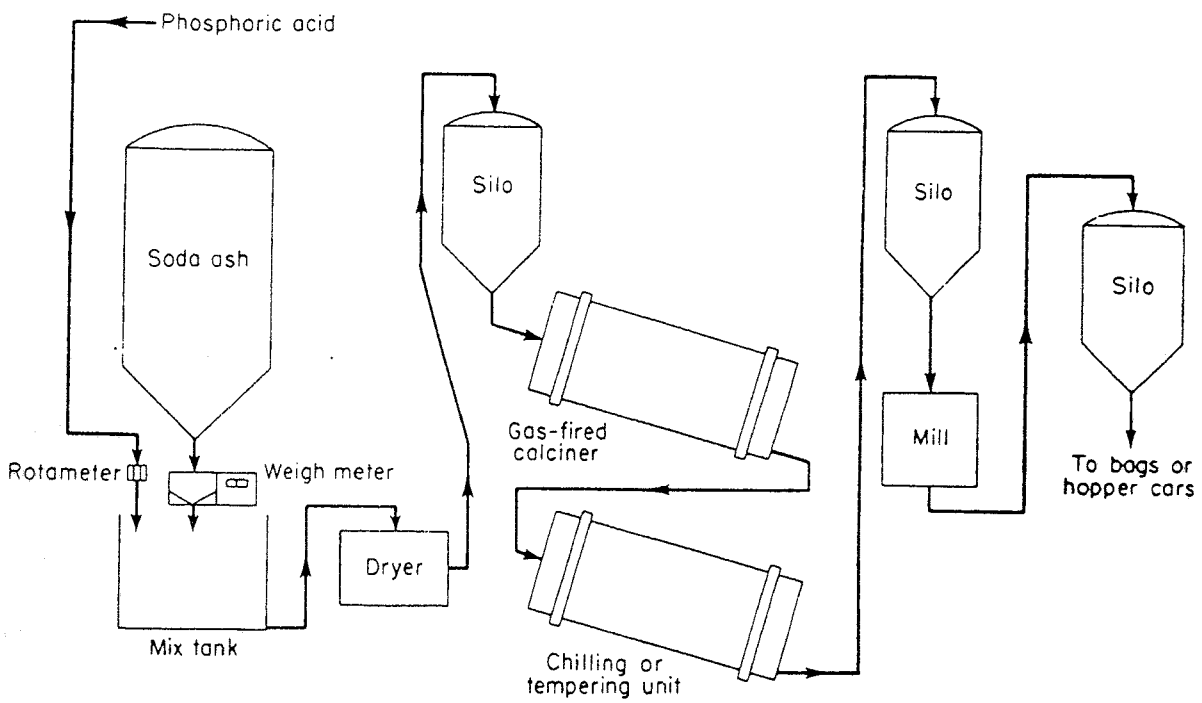


Fig. 1.8. Diagram of a plant for the manufacture of crystalline sodium polyphosphate. *(Thomas L. Hart and John R. VanWazen.)*

soda ash to yield a DSP solution, which may be dried to give anhydrous Na_2HPO_4 or crystallized to give $Na_2HPO_4 \cdot 2H_2O$ or $Na_2HPO_4 \cdot 7H_2O$. These compounds are calcined at a high temperature in an oil- or gas-fired rotary kiln to yield TSPP in a plant such as that shown in Fig. 1.8. The reactions may be written:

$$2Na_2HPO_4 \rightarrow Na_4P_2O_7 + H_2O$$
$$2Na_2HPO_4 \cdot 2H_2O \rightarrow Na_4P_2O_7 + 5H_2O$$

A nonhygroscopic sodium acid pyrophosphate is used extensively as a chemical leavening agent in making doughnuts, cakes, and packaged biscuit doughs. It is manufactured by partially dehydrating monosodium acid orthophosphate at a temperature of 160°C over the course of 6 to 12 h.

$$2NaH_2PO_4 \rightarrow Na_2H_2P_2O_7 + H_2O$$

CALCIUM PHOSPHATES. Monobasic calcium phosphate [$Ca(H_2PO_4)_2 \cdot H_2O$] is manufactured by crystallization, after evaporation and some cooling of a hot solution of lime and strong furnace phosphoric acid. The crystals are centrifuged, and the highly acidic mother liquor returned for reuse. This acid salt is also made by spray-drying a slurry of the reaction product of lime and phosphoric acid. This product is used for baking powder.

Dibasic Calcium Phosphate. Dibasic calcium phosphate, which is used as a polishing agent in dentrifrices, is manufactured from furnace-grade phosphoric acid and lime.

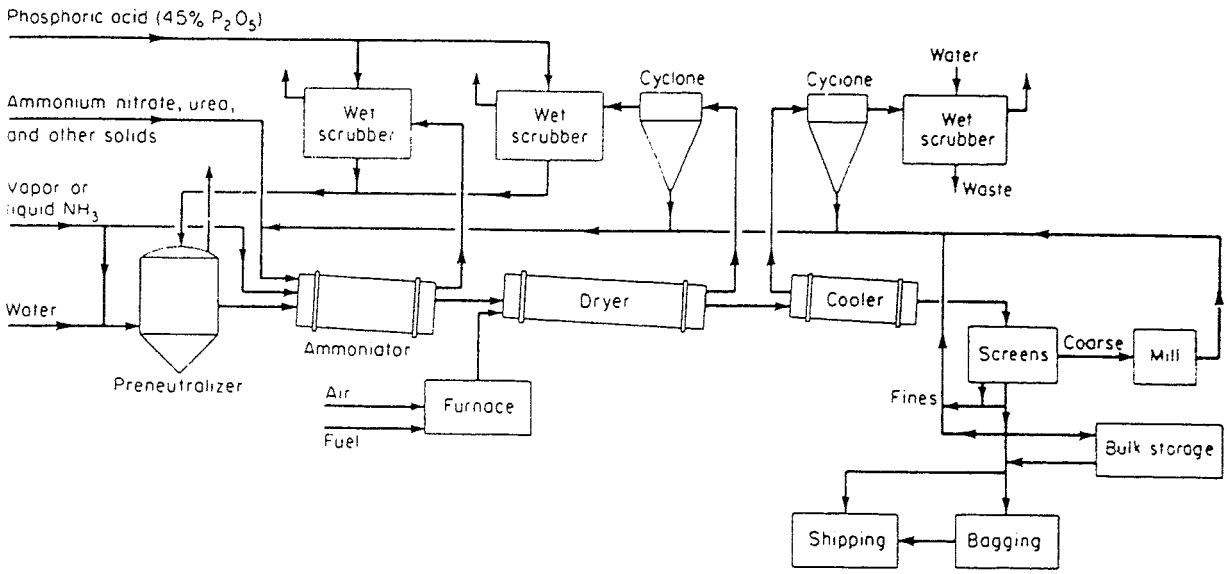
Calcium Metaphosphate. In 1937, the TVA developed a concentrated fertilizer, $Ca(PO_3)_2$, from phosphate rock by the following reaction:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 6P_2O_5 + 2HPO_3 \rightarrow 10Ca(PO_3)_2 + 2HF\uparrow$$

In this process the P_2O_5 contacts the lump rock in a vertical shaft. About 20,000 t of phosphorus equivalent has been manufactured per year. This calcium metaphosphate may be regarded as a dehydrated triple superphosphate made directly from phosphate rock. The calcium metaphosphate is quite insoluble, and it must hydrolyze to become effective:

$$xCa(PO_3)_2 + xH_2O \rightarrow xCa(H_2PO_4)_2$$

GRANULAR HIGH-ANALYSIS FERTILIZER. This is basically a commercial adaptation of the TVA process (Fig. 1.9), designed for the manufacture of diammonium phosphate fertilizer (DAP), either 21-54-0, using furnace phosphoric acid, or 18-46-0, with wet-process phosphoric acid or for any of many grades of granular fertilizer (cf. Chap. 26). The last-mentioned requires the addition of facilities for metering solid raw materials and sulfuric acid to the ammoniator. Vapor or liquid anhydrous ammonia and phosphoric acid (40 to 45% P_2O_5) are metered continuously to an agitated atmospheric tank (preneutralizer) in proportions to maintain a ratio of 1.3 to 1.5 mol of ammonia per mole of phosphoric acid. This ratio is the optimum for maintaining fluidity of the slurry with a minimum quantity of water and a reasonable ammonia loss in the exit vapor from the preneutralizer. In the preneutralizer the heat of reaction elevates the temperature of the mass, evaporating approximately 100 kg of water per metric ton of product. The slurry formed in the preneutralizer flows into a TVA-type ammoniator-granulator at about 120°C, where it is distributed evenly over the bed of



In order to produce 1 t, grade 18-46-0 DAP, the following materials and utilities are needed:

Ammonia	220 kg	Fuel	525 MJ
Phosphoric acid	465 kg	Direct labor	0.5 work-h
Electricity	200 MJ_e		

Fig. 1.9. Flowchart for the manufacture of diammonium phosphate (DAP) or high analysis fertilizer. *(Austin Co.)*

solid material and, for most grades, reacts with additional ammonia fed through a distributor pipe below the surface of the bed to complete the reaction with a molar ratio of 2.0 (diammonium phosphate).[18] Dried recycle material from product screening is used to control the moisture, and additional solid raw materials are metered into the ammoniator, depending on the grade of fertilizer in production. The ammoniator combines the functions of chemical reaction, mixing, and formation of the proper size and shape of granular particles. The moist granules leaving the ammoniator fall into an oil- or gas-fired cocurrent rotary dryer, where the moisture content of the material is reduced to about 1%. The dry product is then cooled by a countercurrent flow of air in a rotary cooler and screened, the coarse material being milled and returned to the ammoniator-granulator. In some plants the cooler is eliminated, and hot screening is used. The fines and, if necessary, some of the product are recycled to the ammoniator to control granule formation and size. The product is conveyed to bulk storage or bagged. The exhaust gases from the dryer and cooler pass through cyclones or a wet scrubber for dust recovery. Exhaust gases from the ammoniator are scrubbed with the incoming phosphoric acid, and in some plants the phosphoric acid stream is split, a portion being used to scrub the vapor from the rotary dryer to minimize ammonia loss.

BAKING POWDERS

The baking-powder industry is an important but indirect consumer of phosphate rock use of leavening agents to produce aeration and lightness in breads and cakes has been [1] since the time of the Egyptians and was handed down by the Greeks and Romans. Le

[18]Chopey, DAP: New Plant Ushers in Process Refinements, *Chem. Eng.* 69 (6) 148 (1962); Pipe Reactor Making Diammonium Phosphate, *Chem. Eng.* 85 (41) 81 (1978).

and unleavened bread are both mentioned in the Bible. Some form of yeast or ferment acting on the carbohydrates in flour, giving CO_2 and an alcohol, was the first leavening agent used. Later, baking soda (sodium bicarbonate) was widely employed but, because it often imparted an unpleasant taste or even a yellowish color due to the alkalinity of the Na_2CO_3 formed, the search for better reagents continued. Baking powders consist of a dry mixture of sodium bicarbonate with one or more chemicals capable of completely decomposing it. The principal "baking acids" used are monocalcium phosphate monohydrate, anhydrous monocalcium phosphate, sodium acid pyrophosphate, sodium aluminum sulfate, tartaric acid, and acid tartrates. Monocalcium phosphates are consumed more than all the others, an estimate being more than 36×10^6 kg annually in the United States. A filler or drying agent, such as starch or flour, is usually added to the active ingredients to give a better distribution throughout the dough and to act as a diluent or to prevent the reaction until water and heat are applied. The following equations represent the actions of different baking powders:

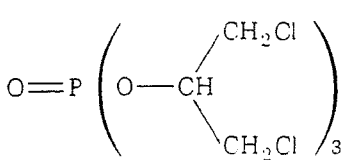
$$Na_2Al_2(SO_4)_4 + 6NaHCO_3 \rightarrow 6CO_2 + 4Na_2SO_4 + 2Al(OH)_3$$
$$3CaH_4(PO_4)_2H_2O + 8NaHCO_3 \rightarrow 8CO_2 + Ca_3(PO_4)_2 + 4Na_2HPO_4 + 11H_2O$$
$$KH_2PO_4 + NaHCO_3 \rightarrow CO_2 + KNaHPO_4 + H_2O$$
$$NaH_2PO_4 + NaHCO_3 \rightarrow CO_2 + Na_2HPO_4 + H_2O$$
$$Na_2H_2P_2O_7 + 2NaHCO_3 \rightarrow 2CO_2 + 2Na_2HPO_4 + H_2O$$
$$KHC_4H_4O_6 + NaHCO_3 \rightarrow KNaC_4H_4O_6 + CO_2 + H_2O$$

Baking powders must yield not less than 12% available CO_2, and most powders contain from 26 to 29% $NaHCO_3$ and enough of the acid ingredients to decompose the bicarbonate and yield from 14 to 15% CO_2. The rest, 20 to 40%, consists of corn starch or flour.

FIRE RETARDANT CHEMICALS

In recent years, there has been a great increase in the use of fire retardants both in flameproofing various textiles, polymeric foams, and for combating forest fires.[19] In 1971 the federal government required the use of flame retardant–treated textiles for the production of children's sleepware, carpets, rugs, mattresses, and mattress pads.[20] A flame retardant enables material to resist burning when exposed to a relatively low-energy ignition source such as a cigarette, match, candle, or stove burner.

After 1971 most of the polyester sleepware for children was made from fabrics treated with tris(2,3 dibromopropyl) phosphate, commonly known as Tris, and tris (dichloroisopropyl) phosphate, Fyrol FR-2.



Fyrol FR-2

[19]Lyons, *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, 1970.

[20]Flammability, *Chem. Eng. News* 56 (17) 22 (1978).

Diethyl N,N-bis (hydroxy) ethylaminomethyl phosphonate (Fyrol 6) is used for the flameproofing of rigid polyurethane foams. For flexible polyurethane foams, Phosgard 2XC20, 2,2-bis (chloromethyl)-1,3 propanediol-[bis(chloroethyl)] phosphate, and Fyrol FR-2 offer excellent flame retardation.

The Consumers Product Safety Commission, acting under the Federal Hazardous Substances Act, banned the use of Tris for children's sleepware in 1977 because some tests had shown that Tris was mutagenic to bacteria, caused kidney cancer in mice and rats, and possibly was carcinogenic to humans. The use of Fyrol FR-2 for this purpose was also adversely affected although this compound had not been shown to be harmful. Large quantities of both compounds are still used for carpets and mattresses.

For combating forest and brush fires, mixtures based on $(NH_4)_2HPO_4$ or $(NH_4)_2SO_4$, thickening agents, coloring matter, and corrosion inhibitors are most commonly used. It is believed that the phosphorus compounds act as catalysts to produce noncombustible gas and char. Furthermore, phosphorus compounds which can yield phosphoric acid from thermal degradation are effective in suppressing glow reactions.[21]

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[21]Lowden et al., *Chemicals for Forest Fire Fighting*, National Fire Protection Association, Boston, Mass. 1963; *User Guide, Phoscheck Fire Retardant*, Monsanto Co., St. Louis, Mo., 1968.

Chapter 2

Potassium Industries

HISTORICAL. The word potash comes from the fact that extraction of wood ashes with water produces a $KOH-K_2CO_3$ solution. Plants selectively remove potassium from soil, acting as potash concentrators and denuding the soil of potassium, which must be replaced if the vegetation is not allowed to decay in the field and thus return potassium to the soil. Early users confused sodium and potassium hydroxides and carbonates, calling them all lye. The German Stassfurt deposits supplied the United States and most of the world with potassium salts from 1869 until World War I. When German supplies were cut off, the price of crude potassium salts rose to $550 per metric ton of 50% muriate (KCl). U.S. production rose from 1000 t (measured as K_2O) of potash in 1915 to 41,500 t in 1919.[1] When the end of the war came, imports were resumed and production fell. Since that time, the discovery of vast new deposits has caused an increase in the amount and quality of potash salts produced. The American deposits are mined mechanically and brought to surface refineries. Solution mining of underground salines promises a lower cost procedure.[1a] Table 2.1 shows statistics concerning potassium salt production. In 1941 and 1942 the United States produced its entire requirement of potash for the first time, and the domestic industry has continued to grow. In 1962, the International Minerals and Chemical Corp. struck rich deposits of potash in Saskatchewan, Canada.[2] Other companies also developed Canadian deposits into major sources of potash.[3] Canadian production is over 3 times U.S. production with the U.S.S.R. producing roughly the same amount as Canada. Canadian production is almost exclusively KCl; U.S. production includes much K_2SO_4. As a consequence, although the U.S. has imported over half its requirements since 1971 (77 percent in 1980), there is a brisk U.S. export business in potassium salts.

Potassium salts are preferred over sodium salts for laboratory and pyrotechnic work because they are less hygroscopic, form fewer and simpler hydrates, and the hydrates formed are more stable to heat. For industrial purposes, these values rarely offset the substantial additional cost.

POTASSIUM

Metallic potassium was first prepared by H. Davy in 1807 by electrolysis of fused KOH. It is similar to sodium but more reactive. It is not widely used. Commercially it is not prepared

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[1] t = 1000 kg.

[1a] Piombino, *Chem. Week* 93 (11) 73 (1963); Potash Minerals, *Chem. Eng. Prog.* 60 (10) 19 (1964).

[2] Canadian Potash Heads for Market, *Chem. Week* 90 (25) 31 (1962); Potash: a Little Tight Now, Ample by 1983, *Chem. Week* 127 (26) 28 (1980).

[3] *Minerals Yearbook*, vol. 1, U.S. Bureau of Mines, 1980.

Table 2.1 Statistics on Potassium Salts (in thousands of metric tons and thousands of dollars)

	1970	1976	1978	1979	1980	1981
United States						
Production of K salts	4,412	4,016	4,326	4,271	4,315	4,153
K_2O equivalent	2,481	2,177	2,253	2,225	2,239	2,159
Sales of K salts by producers	4,855	4,184	4,358	4,549	4,265	3,670
K_2O equivalent	2,426	2,268	2,307	2,388	2,217	1,908
Value at plant, $	92,373	210,800	226,500	279,200	353,900	328,900
Average value, per metric ton, $	21.60	50.37	51.97	61.38	82.98	89.62
Exports of K salts*	878	1,514	1,431	1,119	1,584	887
K_2O equivalent*	495	857	809	635	840	491
Value, $	28,473	91,900	88,600	79,500	179,830	107,950
Imports of K salts for use	3,569	6,875	7,762	8,505	8,193	7,903
K_2O equivalent*	2,368	4,168	4,707	5,165	4,972	4,796
Customs value, $	60,703	344,000	399,000	520,800	648,000	750,400
Apparent consumption of K salts	7,400	9,544	10,689	11,935	10,874	10,686
K_2O equivalent	4,300	5,578	6,205	6,918	6,349	6,213
World						
Prod'n., marketable, K_2O equivalent	18,194	24,281	26,113	25,677	27,673	27,357

*Excludes potassium chemicals and mixed fertilizers.

SOURCE: *Minerals Yearbook 1981*, Dept. of the Interior.

by electrolysis of fused KCl because K attacks the electrodes and tends to remain dispersed in the fused salt. Instead it is prepared from KCl by double decomposition with sodium:[4]

$$Na + KCl \leftrightharpoons K + NaCl$$

It is used in the high-temperature heat transfer alloy "NaK" and for the manufacture of KO_2, the dioxide used in life-support systems. It must be stored under an unreactive gas such as nitrogen.

RAW MATERIALS. The largest domestic production of potassium salts has come from deep Permian sedimentary deposits of sylvinite [a natural mixture of sylvite (KCl) and halite (NaCl)] and langbeinite ($K_2SO_4 \cdot 2MgSO_4$) near Carlsbad, N.Mex. The sylvinite is mined and treated to yield high-grade potassium chloride, and langbeinite is processed to make potassium sulfate. Another domestic source of potassium salts is Searles Lake at Trona, Calif., which is a deposit of solid sodium salts permeated by a saturated complex brine. This brine is processed to separate high-grade potassium chloride and borax, together with numerous other saline products (Figs. 2.1 to 2.4). Deposits of KCl at Moab, Utah, are being solution

[4]Jackson and Werner, U.S. Patent 2,480,655 (1949).

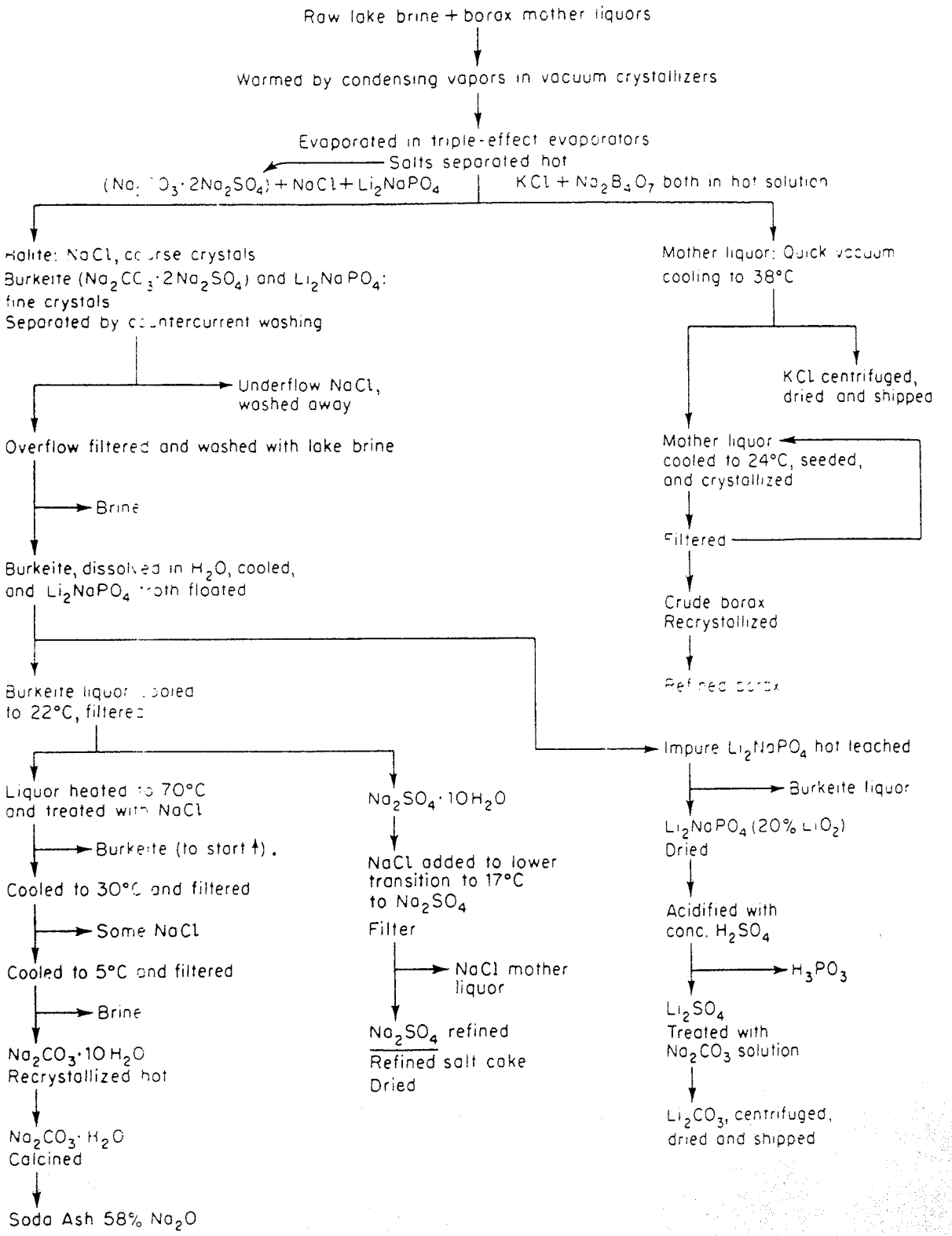

Fig. 2.1. Outline of Trona procedures. (See Chap. 20, Boron Compounds.)

mined. Great Salt Lake brines are being treated by solar evaporation to produce K_2SO_4 along with other minerals, but the project is encountering difficulties. Worldwide, currently 79 percent of all potassium salt production[5] is KCl and 9 percent K_2SO_4. In the United States, New Mexico mines produced 74 percent of total production, mostly K_2SO_4 (1980). Worldwide,

[5] *Minerals Yearbook*, vol. 1, U.S. Bureau of Mines, 1980.

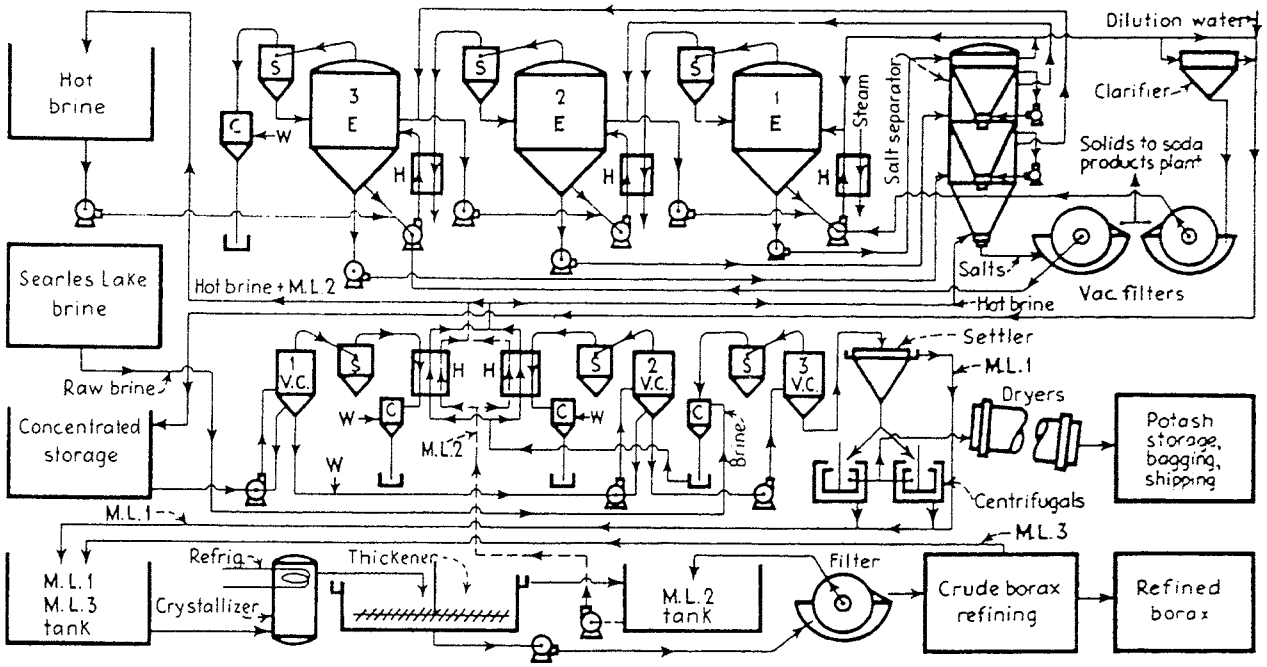

Fig. 2.2. Potassium chloride and borax by the Trona procedure. (See Fig. 17.1 for supplementary details.) *Key:* C. barometric condenser; E, evaporator; H, heater or heat exchanger; M.L., mother liquor; S, separator; V.C., vacuum crystallizer; W, cooling or dilution water.

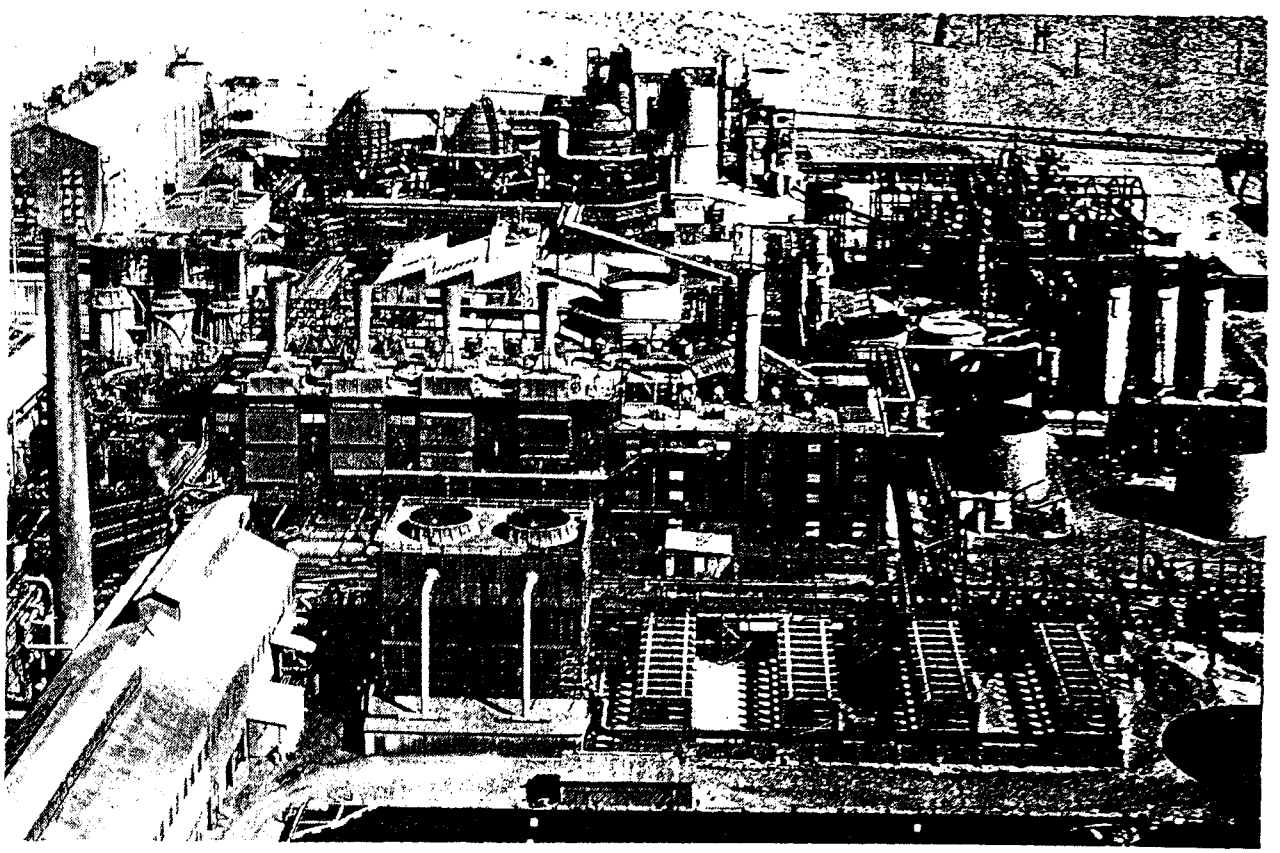

Fig. 2.3. Trona: overall view of the plant with large evaporators in the back. *(American Potash & Chemical Corp.)*

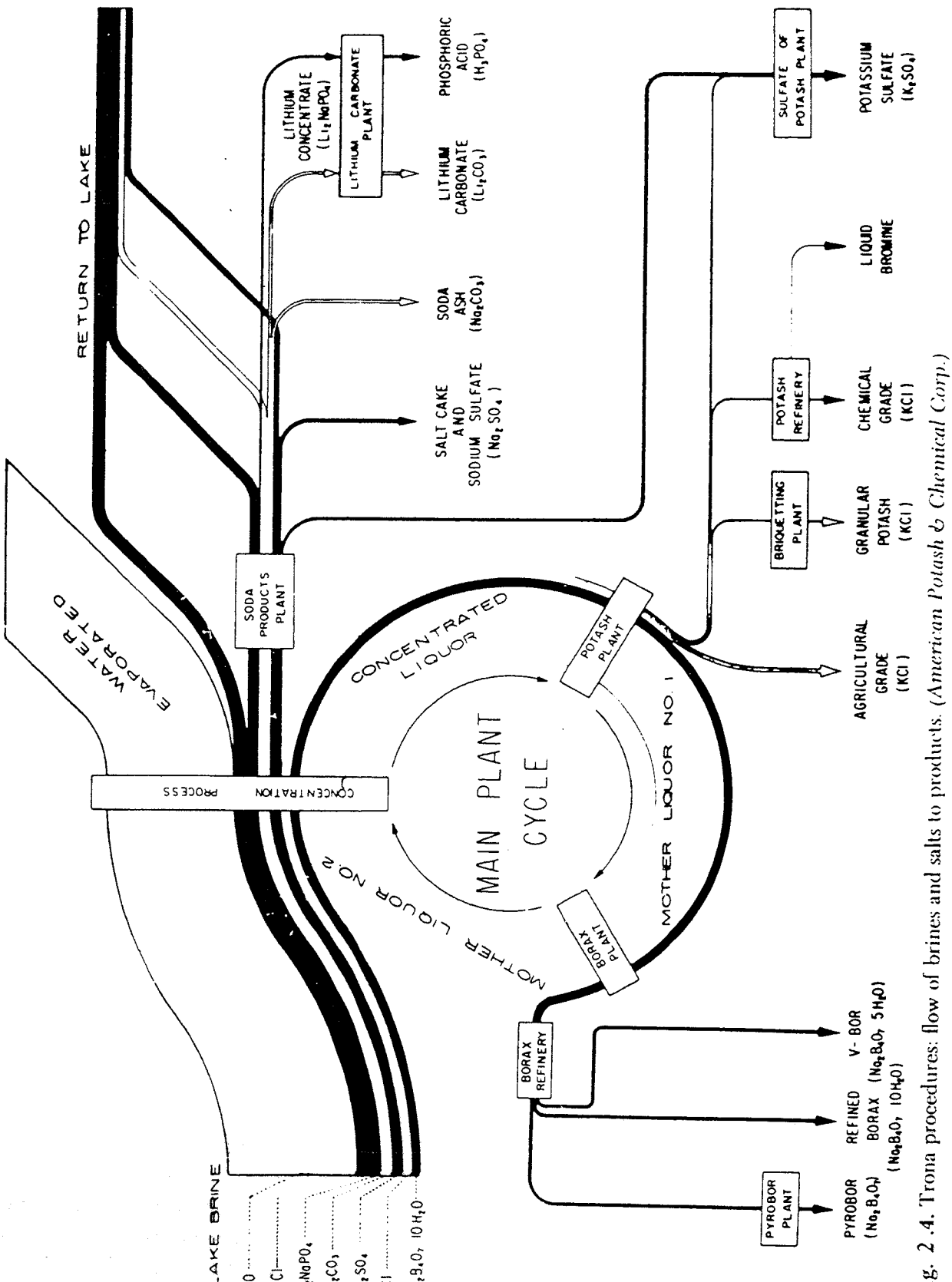

Fig. 2.4. Trona procedures: flow of brines and salts to products. (*American Potash & Chemical Corp.*)

major producers are (parentheses show millions of metric tons of K_2O produced): U.S.S.R. (7.6), Canada (7.3), East Germany (3.2), West Germany (2.3), United States (2.2), France (1.8), and others (1.7). Israel and Jordan are building plants on the Dead Sea which are expected to have large capacities. Brazil and China also are producers of increasing quantities. Since sodium and potassium are of about equal abundance in the earth's crust, the distribution of potassium salt deposits is wide. It is strange that the seas contain so little potassium; this is accounted for by the great affinity of both soil and plants for potassium compounds.

POTASSIUM CHLORIDE

In this country about 90 percent of the potassium chloride is produced as fertilizer grade of about 97% purity. In the fertilizer trade it is referred to as *muriate of potash.* The chemical grade, or 99.9% potassium chloride, is the basis of the manufacture of most potasium salts.

MANUFACTURE BY THE TRONA PROCESS. From Searles Lake, Calif., the shipping of potash was begun in 1916 and, including numerous other products, has continued since that time on an ever-expanding scale. The lake is composed of four layers. The upper layer of crystalline salt is from 20 to 30 m deep; the second layer, about 4 to 5 m of mud; the third layer, about 8 m of salt; and the bottom layer is mud interspersed with minor salt seams. In processing, the brine is pumped from the interstices in the salt body from the first and third layers. The brines have the following approximate constant composition:

Expressed As	Upper Deposit, %	Lower Deposit, %
KCl	4.85	3.00
NaCl	16.25	16.25
Na_2SO_4	7.20	6.75
Na_2CO_3	4.65	6.35
$Na_2B_4O_7$	1.50	1.77
Na_3PO_4	0.155	
NaBr	0.109	
Miscellaneous	0.116	0.35
Total salts (approx.)	34.83	34.60
H_2O	65.17	65.40
Specific gravity	1.303	1.305
pH (approx.)	9.45	9.60

As determination of the composition of the various salts from the German potash deposits at Stassfurt by van't Hoff from 1895 to 1910 helped greatly in the development of the German potash industry, likewise the phase-rule study[6] of the much more complex systems existing at

[6]Teeple, *Industrial Development of Searles Lake Brines*, Reinhold, New York, 1929; Robertson, The Trona Enterprise, *Ind. Eng. Chem.* **21** 520 (1929); Expansion of the Trona Enterprise, *Ind. Eng. Chem.* 34 133 (1942); Gale, Chemistry of the Trona Process from the Standpoint of the Phase Rule, *Ind. Eng. Chem.* 30 867 (1938). The triangular phase diagrams of the more common constituents of Searles Lake brine at 20 and 100°C are presented and described in Kobe, *Inorganic Chemical Processes*, Macmillan, New York, 1948, pp. 71–74ff. These are for the brines saturated with NaCl at all points and for burkeite, Na_2SO_4, glaserite, KCl, and Na_2CO_3.

Searles Lake by Morse, Teeple, Burke, Mumford, Gale, and many others was another striking investigation carried to successful application in the Trona process. In the first-layer brine of Searles Lake the main system is $Na–K–H–SO_4–CO_3–B_2O_4–Cl–F–H_2O$. The references cited, particularly the one by Gale, demonstrate with appropriate solubility charts this important and commercial application of the phase rule, wherein the conditions are presented for the desired fractional crystallization.

The chemists and engineers at Trona have been ingenious in obtaining pure salts from this complex brine and in building a profitable industry in a competitive field and under the handicap of being in the desert 320 km from the nearest major city. The town of Trona, Calif., houses more than 2000 inhabitants dependent on this one industry. Figure 2.1 outlines the steps, based on the phase-rule study, necessary to commercialize this brine. Figure 2.2 gives more details of the division of the procedures leading to potassium chloride, borax, and soda products. There is no profitable market for the large tonnages of common salt obtained, and it is washed back into the lake.

In general, this successful process is founded upon many years of intensive research wherein exact conditions were worked out and then applied in the plant. In barest outline this involves the concentration of potassium chloride and borax in hot brine and the simultaneous separation of salt and burkeite, a new mineral with the composition $Na_2CO_3 \cdot 2Na_2SO_4$. By virtue of the delayed crystallization of borax, potassium chloride can be obtained by rapid cooling of the concentrated brine in vacuum coolers and crystallizers.[7] After centrifugation, the potash mother liquor is refrigerated and furnishes borax.

The somewhat detailed[8] flowchart in Fig. 17.2 can be resolved into the sequences that follow.

Concentration and soda-products separation

Raw brine is mixed with end liquors from the borax crystallizing house and pumped into the third effect of triple-effect evaporators.

The brine is hot-concentrated, and salted out in the three effects counter to the steam flow (Figs. 2.3 and 2.4).

The suspended salts, NaCl and $Na_2CO_3 \cdot 2Na_2SO_4$, are removed from the liquors of each effect by continuously circulating the hot liquor through cone settlers called *salt separators*, or *salt traps*. The underflow from the first-effect cone containing the salts passes through an orifice into the second-effect cone, receiving a countercurrent wash with clarified liquor from the second-effect cone. The combined salts from the first and second cones are given a countercurrent wash with liquor from the third cone as they pass through an orifice into their third cone. The combined salts of the first, second, and third cones receive a countercurrent wash with raw brine as they leave the third-effect cone. All these are hot washes. The combined underflow is filtered, and the filtrate returned to the evaporators.

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[7]Perry, 5th ed., pp 17-8 to 17-19; Turrentine, *Potash in North America*, Reinhold, New York, 1943. (The first vacuum cooler-crystallizer is pictured and described.) Turrentine's invention has had a profound influence upon the cheap production of pure potassium chloride both in the United States and abroad.

[8]Mumford, Potassium Chloride from the Brine of Searles Lake, *Ind. Eng. Chem.* 30 872 (1938); Kirkpatrick, A Potash Industry; at Last, *Chem. Met. Eng.* **45** 488 (1938); Searles Lake Chemicals, *Chem. Met. Eng.* **52** (10) 134 (1945).

The cake (salt: NaCl and $Na_2CO_3 \cdot 2Na_2SO_4$) is sent to the soda-products plant (middle lower part of Fig. 2.1).

The final hot, concentrated liquor is withdrawn from the overflow of the first-effect cone into an auxiliary settler called a clarifier. The overflow from the clarifier is pumped to storage at the potash plant.

The underflow from the clarifier is filtered and treated in the same manner as the previous underflow.[9]

Separation of potassium chloride

The hot, concentrated liquor leaving the clarifiers is saturated with potassium chloride and borax. The potassium chloride is obtained by cooling quickly to 38°C and crystallizing in three-stage vacuum cooler-crystallizers.

Enough water is added to replace that evaporated so that the sodium chloride remains in solution.

The suspension of solid potassium chloride in the mother liquor is passed to a cone settler, where the thickened sludge is obtained as the underflow.

The potassium chloride is dried in rotary driers, yielding 97% potassium chloride. This salt is conveyed to storage, to the bagging plant, or to a recrystallizing procedure.

Separation of borax[10]

The overflow, combined with the filtrate, is pumped to the borax plant for removal of borax.

The potash mother liquor is cooled in vacuum crystallizers as shown in Fig. 17.2. The water lost by evaporation is returned to the boiling (but cooling) solution to prevent the concentration of this solution with consequent crystallization of potassium chloride with the crude borax.

The borax crystallizes out as a crude sodium tetraborate pentahydrate.

The crude borax is filtered off and washed.

The filtrate is returned to the start of the evaporator cycle.

When necessary, the crude borax is refined by recrystallization.

This salt is centrifuged, dried, and packaged for market.

The preceding description deals with the processing of the upper brine layer. In 1948 a new plant was finished at Trona for the lower brine layer. The process used involves carbonation of this brine with flue gas from the boiler plant.[11] The sodium bicarbonate separated by this reaction is calcined and converted to dense soda ash. Crude borax is crystallized from the carbonated end liquor by cooling under vacuum, and the filtrate is returned to the lake. The daily production of American Potash and Chemical Co. is approximately 525 t of muriate of potash, with borax, boric acid, salt cake, and soda ash as coproducts. Evaporation is at the rate of several million kilograms of water per day. To effect the requisite heat transfer when

[9]Mumford, op. cit., pp. 876, 877; Hightower, The Trona Process, *Chem. Eng.* 58 (8) 104 (1951) (excellent flowcharts).

[10]See Chap. 20 for boron compounds for the *solvent extraction* of boric acid from Searles Lake brine and from borax mother liquors.

[11]Hightower, New Carbonation Technique: More Natural Soda Ash, *Chem. Eng.* 58 (5) 162 (1951); 56 (4) 102 (1949).

salts crystallize out at the same time was a major chemical engineering problem. This problem was solved by removing the piping from inside the evaporators and doing the heating in outside heaters under mild hydrostatic pressure with minimum evaporation.[12] The superheated solution is flashed into evaporators. Heat transfer is also facilitated by vacuum cooling through vaporization instead of using cooling liquids in coils, which would become fouled with encrusted solids. The increased cost of energy has resulted in careful analysis of the processes and led to substantial reduction in energy use, but the actual changes made have not yet been disclosed.

The extraction of *soda and lithium products*[13] is a development resulting from an extension of the phase studies. Figure 2.1 outlines the production of soda ash, anhydrous sodium sulfate, and lithium carbonate. Figure 2.4 diagrams the flow of brines and salts at Trona.

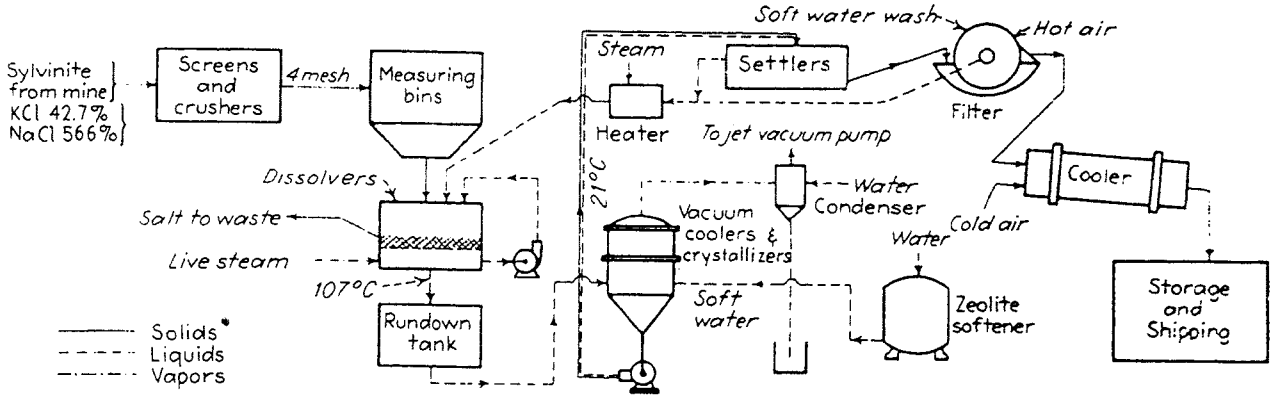
MANUFACTURE FROM SYLVINITE. In 1925 potash was discovered at Carlsbad, N.Mex.[14] After much prospecting and drilling, a shaft to mine the mineral was sunk to about 300 m, and in 1932 a refinery was constructed.

The process employed by the United States Borax and Chemical Corp. depends primarily upon the fact that sodium chloride is less soluble in a hot than in a cold saturated solution of potassium chloride. Thus, when a saturated solution of the mixed salts in water is cooled from its boiling point, potassium chloride separates out, contaminated with only the sodium chloride that is entrained. The cold mother liquor is heated to 110°C by the use of heat exchangers employing exhaust steam, as shown in Fig. 2.5. The hot mother liquor is passed through a series of steam-heated turbomixer dissolvers countercurrent to a flow of ore crushed to −4 mesh size, which is moved from dissolver to dissolver by mechanical elevating equipment. The potassium chloride goes into solution, together with a small amount of sodium chloride. In this step colloidal and semicolloidal clays present in the ore are suspended in the potash-bearing solution. The enriched mother liquor passes through thickener equipment, where this insoluble mud settles out. The underflow mud is washed by countercurrent decantation in a tray thickener, and the not-clear, saturated overflow solution is pumped to vacuum coolers and crystallizers. Tailings from this process, largely sodium chloride, after passing through Bird centrifuges where adhering potash-bearing brine is removed, are carried out of the plant to waste storage. Vacuum in the coolers and crystallizers is maintained by means of steam ejectors. In these vessels the solution is cooled to 27°C, and the potassium chloride comes out of solution and, in suspension, is pumped to settling tanks where a large part of

[12]Manning, Capital + Vision + Research = An American Potash Industry, *Chem. Met. Eng.* **36** 268 (1929).

[13]Reburn and Gale, The System Lithium Oxide–Boric Oxide–Water, *J. Phys. Chem.* **57** 19 (1955); Robertson, Expansion of the Trona Enterprise, *Ind. Eng. Chem.* 34 133 (1932); Gale, Lithium from Searles Lake, *Chem. Ind.* 57 422 (1945); Salt Lake Projects, *Chem. Eng. News* **46** (16) 11 (1968); Potash, *Chem. Week* **105** (21) 36 (1969).

[14]Smith, Potash in the Permian Salt Basin, *Ind. Eng. Chem.* **30** 854 (1938). For the separation of two salts with a common ion, like NaCl–KCl, see the phase diagrams figs. 3-1 and 3-2 of Kobe, *Inorganic Process Industries*, Macmillan, New York, 1948; Ullmann, *Enzyklopaedie der technischen Chemie*, vol. 9, 1957, p. 187 (phase diagrams and flow diagrams); Gaska et al., Ammonia as a Solvent (to prepare pure KCl from NaCl, KCl), *Chem. Eng. Prog.* **61** (1) 139 (1965).



In order to produce 1 t of refined KCl, the following materials and utilities are required:

Sylvinite	2.51 t	Electricity	180 MJ
Water	170–200 m^3	Direct labor	4–5 work-h
Steam	1250 kg		

Fig. 2.5. Potassium chloride (muriate) from sylvinite, with continuous flow dissolving for hot-solution refining. *(U.S. Potash Corp.)*

the liquor is decanted through launders to be used again. The thickened crystal mass is filtered, washed, and dried on Oliver filters. The dried cake is crushed, screened, and conveyed either to a warehouse or to cars.

A plant for producing granular 50% potassium chloride, used almost entirely by the fertilizer industry, operates as follows. Crushed and sized ore suspended in a brine saturated with both sodium and potassium chloride is carried to a bank of Wilfley tables, where sodium chloride and potassium chloride are separated by their difference in gravity. A product carrying 50 to 51% K_2O is debrined in drag classifiers and passed through gas-fired rotary dryers, from which it goes to storage and shipping. A middling product is further tabled after debrining, and the tailing is debrined and carried to a salt-storage pile.

The process of the Potash Company of America separates potassium chloride from sodium chloride chiefly by a metallurgical concentration method using a *soap-flotation* process and represents the first adaptation to water-soluble ores of the flotation principle so long familiar in the concentration of insoluble ores. The sylvinite ore, having been coarsely crushed underground, is fed to an intermediate crusher, which in turn discharges to fine crushers. The ore is then wet-ground by ball mills to 100 mesh. The mill product is treated in two series of flotation cells to float off an NaCl concentrate and depress a KCl concentrate. The NaCl crystals are washed and separated from the solution by means of a thickener and a filter and sent to waste while the KCl concentrate, together with KCl crystals recovered from various circulating solutions, is separated by a classifier into fine and coarse fractions. Recovery of fines is accomplished by a thickener and centrifuges.

The *flotation* process is used also by International Minerals and Chemical Corp. in the refining of sylvinite to produce potassium chloride. This company also processes potassium sulfate from the mineral langbeinite ($K_2SO_4 \cdot 2MgSO_4$) by reacting it with potassium chloride to yield the sulfate and the by-product magnesium chloride. The latter is of particular interest as a raw material for the production of metallic magnesium, potassium chloride, and sulfate of potash-magnesia. Great Salt Lake minerals have also been separated by a flotation process[15]

[15]Tippin, Potash Flotation Method Handles Variable Feed, *Chem. Eng.* 84 (15) 73 (1977).

using an anionic short-chain, saturated fatty acid collector to float schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$).

POTASH FROM SASKATCHEWAN, CANADA. This is North America's major source of supply. It is estimated that it will satisfy the world potash demand for more than 600 years. It is, however, deep down—1100 or more meters—and layers of water-soaked deposits and quicksand must be penetrated. This was accomplished by the International Minerals and Chemical Corp.[16] It proved to be America's toughest mining venture and involved solidifying 90 m of the prospective 6-m-diameter shaft area by refrigeration with lithium chloride brine. About 1½ years was required to freeze through the 61 m of quicksand, after which the shaft was dug and then lined with cast-iron circular segments at a cost of $2 million. The installation of hoisting machinery followed.

The refinery for processing the raw salts from the mine has been operating[17] since 1963. The ore is sylvinite ($xNaCl \cdot KCl$) and carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) (Fig. 2.6). The International Minerals and Chemical Corp. process as depicted grinds and sizes the ore. This ore is treated with a brine which leaches out the carnallite, deslimes the ore, and then separates the potassium salts into fines and coarse material. After this separation, the fines are deslimed by a hydroseparator, treated with an amine and starch, and combined with the coarse salts, which are similarly treated. Both the fines and the coarse salts are conducted to flotation cells to separate the potassium salts from the sodium chloride by flotation. When the ore is treated with the brine, the carnallite is decomposed, dissolving the magnesium chloride, and the potassium chloride begins to crystallize. Fresh water added continuously prevents the brine from becoming saturated with magnesium chloride. Although some potassium chloride dissolves, the main brine effluent carries mostly sodium chloride and potassium chloride.

Fertilizer Use. Over 90 percent of potash salts mined enter the fertilizer field, mostly as mixed fertilizers. These are presented in Chap. 26 on agrichemicals.

POTASSIUM SULFATE

Prior to 1939, the German potash industry was the chief source of potassium sulfate for the American chemical and fertilizer industries, although considerable tonnages were being produced in this country by the interaction of potassium chloride and sulfuric acid as a coproduct of salt-cake manufacture. With the termination of European imports, the production of the salt was undertaken on a larger scale by the American Potash and Chemical Corp. through the interaction of burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) with potassium chloride, followed in turn by the successful recovery of this salt from langbeinite by the International Minerals and Chemical Corp. In agricultural use potassium sulfate is preferred for the tobacco crop of the southeast and the citrus crop of southern California.

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[16]Potash Industry, *Chem. Eng. News* **46** (38) 20 (1968); Potash, *Chem. Week* **127** (26) 28 (1980).

[17]Cross, World's Largest Supply Feeds New Potash Plant, *Chem. Eng.* **69** (23) 176 (1962) (flowchart, pictures, description); Gaska et al., Ammonia as a Solvent (for NaCl, KCl), *Chem. Eng. Prog.* **61** (1) 139 (1965)

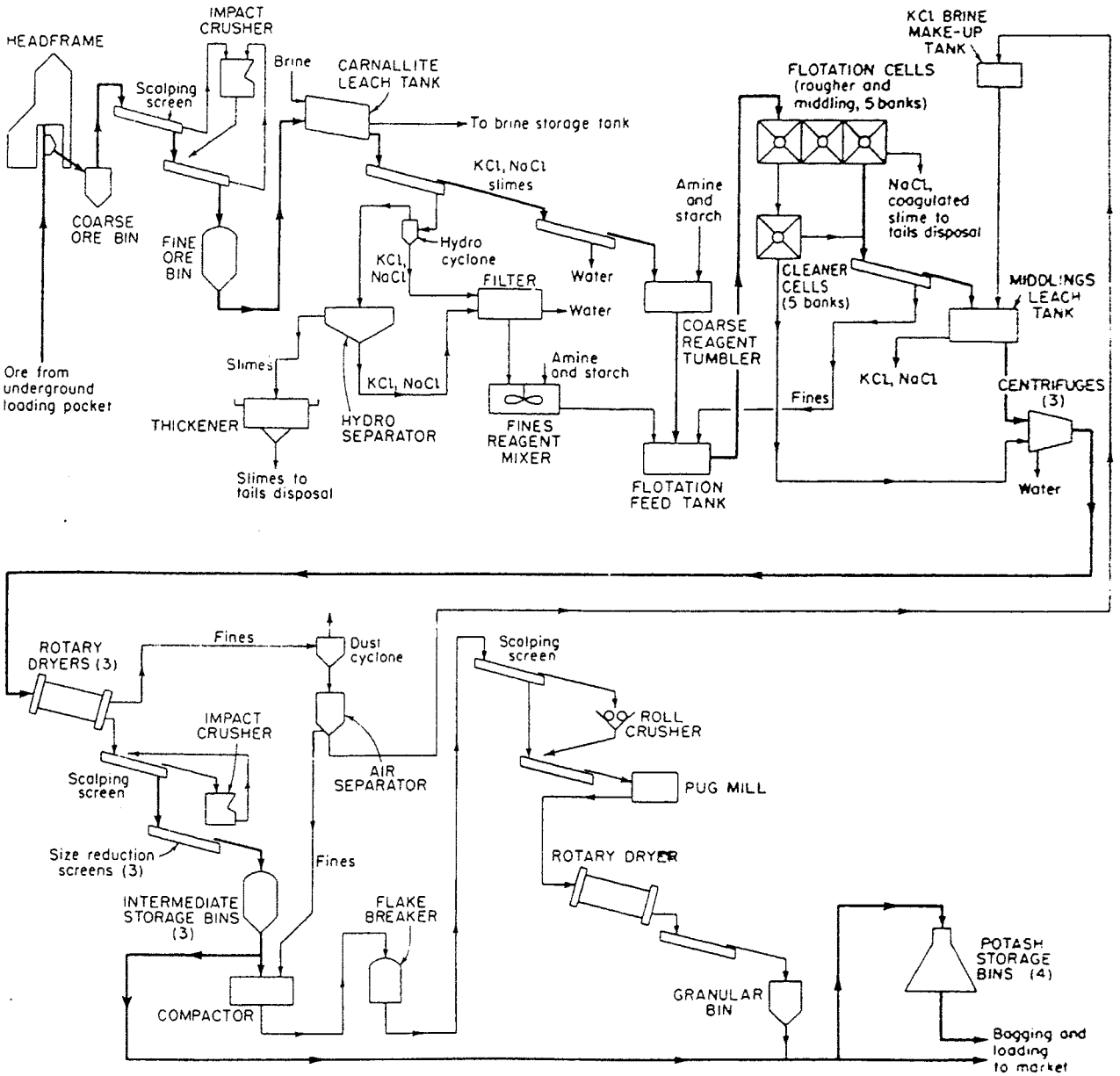

Fig. 2.6. Potash mine and refinery. Banks of flotation cells separate potash particles from NaCl. [*International Minerals & Chemical Co., Esterhazy, Saskatchewan, Canada; Chem. Eng.* 68 *(23) 176 (1962).*]

POTASSIUM BISULFATE

Potassium bisulfate is readily prepared from K_2SO_4 by reaction with sulfuric acid. It is a strongly acidic material and is used as a flux for ceramics.

POTASSIUM HYDROXIDE

Potassium hydroxide (caustic potash) is made by the electrolysis of KCl using procedures similar to those for NaOH. Some electrolytic plants shift back and forth between KOH and

NaOH to meet market demands. Five U.S. producers made 357,000 t in 1981. Of this, 25 percent was converted to potassium carbonate, 17 percent used to make liquid fertilizers, 10 percent reacted to form potassium phosphates, and 6 percent used for potassium permanganate; the rest went into pesticides and other chemicals.

POTASSIUM CARBONATE

Potassium carbonate (pearl ash) is made by reacting caustic potash with carbon dioxide. This is the preferred source of potash for hard glass. It is also used for making pottery, smalts, and soaps; for engraving processes; for finishing leather; and as an absorbent for acid gases (CO_2 and H_2S).

POTASSIUM BROMIDE

Potassium bromide is the classical sedative, but now its greatest use is in photographic emulsions and photoengraving. It is made by first forming iron bromide by the reaction of liquid bromine and scrap iron (usually stampings or borings). This is then reacted with K_2CO_3 (sometimes KOH) to form the salt, which is filtered and crystallized.

$$3Fe + 4Br_2 \rightarrow Fe_3Br_8$$

$$Fe_3Br_8 + 4K_2CO_3 + 4H_2O \rightarrow 8KBr + 2Fe(OH)_3 + Fe(OH)_2 + 4CO_2$$

POTASSIUM IODIDE

Potassium iodide is made in essentially the same way as KBr, except that iodine is used to dissolve the iron. It is valuable for photographic use, in animal and human feed (particularly to make iodized salt), and in pharmaceutical preparations.

POTASSIUM NITRATE

Potassium nitrate, once in great demand as a constituent of black powder, is now used more prosaically as a fertilizer, in pyrotechnic mixtures, as a heat-transfer medium (as a eutectic mixture with $NaNO_2$), for heat-treating steel, and in foods. Originally recovered from spots where bacterial action on human and animal manure had formed it and evaporation made it crystalline (Parisian cellars and Indian stables), it later was recovered from Chile saltpeter, which is about 10% potassium nitrate. It is now usually made by double decomposition between $NaNO_3$ and KCl:

$$NaNO_3(aq) + KCl(s) \rightarrow NaCl\ (s) + KNO_3(aq) \qquad \Delta H = +\ 13.2\ kJ$$

A strong, hot solution of $NaNO_3$ is made, and solid KCl is dumped into the kettle. Upon heating, the KCl crystals change to NaCl crystals, and the hot potassium nitrate solution is run through the NaCl crystals at the bottom of the kettle. A little water is added to prevent further deposition of NaCl as the solution is cooled. A good yield of potassium nitrate results. The Southwest Potash Co.[18] makes potassium nitrate at its fertilizer plant at Vicksburg. Miss., reacting KCl from the company's Carlsbad plant with nitric acid to furnish 63,000 t/year of potassium nitrate and 22,000 t of chlorine.[19]

$$2KCl + 2HNO_3 + \tfrac{1}{2}O_2 \rightarrow 2KNO_3 + Cl_2 + H_2O$$

The step-by-step reactions are:

$$\text{Step 1: } 3KCl + 4HNO_3 \xrightarrow{100°C} 3KNO_3 + NOCl + Cl_2 + 2H_2O$$
$$\text{Step 2: } NOCl + 2HNO_3 \longrightarrow 3NO_2 + \tfrac{1}{2}Cl_2 + H_2O$$
$$\text{Step 3: } 2NO_2 + H_2 + \tfrac{1}{2}O_2 \longrightarrow 2HNO_3$$

The key process features are (1) a shift in the composition of the nitric acid–water azeotrope from about 70% HNO_3 to over 80% HNO_3, in the presence of KNO_3 at high concentration, and (2) the capability of oxidizing nitrosyl chloride to Cl_2 and NO_2 with nitric acid in the 70 to 80% concentration range at temperatures and pressures that are practical for operation. Potassium nitrate made in this fashion is nearly competitive with potassium sulfate as a source of potassium and nitrogen and is preferred over KCl for plants, such as tobacco, that are adversely affected by chloride in the soil.

Black powder is no longer a military propellant but is essential as an igniter for smokeless powder and as the combustible in slow-burning fuses.

POTASSIUM ACID TARTRATE (Bitartrate)

Pomace, the fruit residue left after pressing fruits for juice, and argols, the precipitate formed in wine vats, are processed for the domestic production of potassium acid tartrate. Crude argols are also imported. Leaching and crystallization produce the commercial salt. As *cream of tartar* it is used in some types of baking powder, in medicine, and as the K, Na salt in crystals for electronic use.

POTASSIUM PERMANGANATE

Potassium permanganate can be made by passing CO_2 through a potassium manganate solution, which is made by treating MnO_2 with KOH and O_2. This much-favored laboratory

[18]Nitrate Potash, *Chem. Eng.* **71** (1) 44 (1964).

[19]Spealman, New Route to Chlorine and Saltpeter, *Chem. Eng.* **72** (23) 198 (1965) (flowchart and details); Mehring et al., Potassium Nitrate, *Ind. Eng. Chem.* **21** 379 (1929); Synthetic Saltpeter Scores, *Chem. Week* **97** (4) 35 (1965).

reagent is far too expensive to use as a commercial oxidizing agent and is made only in small quantity.

POTASSIUM DICHROMATE

Potassium dichromate (bichromate) is another expensive oxidizing agent with a few specialized industrial uses which can usually be filled by the less expensive sodium salt. It is made by roasting caustic potash, quicklime, and chrome-iron ore:

$$4Fe(CrO_2)_2 + 8K_2CO_3 + 7O_2 \rightarrow 8K_2Cr_2O_7 + 2Fe_2O_3 + 8CO_2$$

The quicklime serves only to keep the melt porous so air can enter and react. It can also be made by reacting sodium dichromate with KCl.

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Chapter 3

Nitrogen Industries

Fixed nitrogen from the air is the major ingredient of fertilizers which make intensive food production possible. During the development of inexpensive nitrogen fixation processes, many principles of chemical and high-pressure processes were clarified and the field of chemical engineering emerged. Before synthetic nitrogen fixation, wastes and manures of various types, or their decomposition products, and ammonium sulfate as a by-product from the coking of coal were the primary sources of agricultural nitrogen. They were messy and insufficient to meet needs. Chilean saltpeter, saltpeter from human and animal urine, and later ammonia recovered from coke manufacture became important, then were replaced by synthetic ammonia and nitrates. Ammonia is the base from which virtually all nitrogen-containing products are derived.

HISTORICAL. Priestly and Cavendish passed electric sparks through air and produced nitrates by dissolving the oxides of nitrogen thus formed in alkalies. Commercial development of this process has proved elusive, for much electrical energy is consumed at low efficiency. Nitrogen has been fixed as calcium cyanamide, but the process is too expensive except for producing chemicals requiring the cyanamide configuration. Other processes, such as thermal processing to mixed oxides of nitrogen (NOX), cyanide formation, aluminum nitride formation, and decomposition to ammonia, etc., show little commercial promise although they are technically possible. Haber and Nernst made careful studies of the equilibrium between nitrogen and hydrogen under pressure to form ammonia and discovered several suitable catalysts. No high-pressure apparatus was then available, and they had to invent as they went along. Haber and Bosch also worked out processes for obtaining inexpensive pure hydrogen and nitrogen by workable processes. The obvious electrolysis of water for hydrogen production and the distillation of liquid air to provide nitrogen proved unduly expensive, so they derived other, better processes. These cooperative efforts made the commercial high-pressure synthesis of ammonia possible by 1913. This energy-intensive process has undergone considerable modification in recent years, resulting in prices which have not escalated as rapidly as energy prices in general. Major improvements are very recent and are continuing at a fast pace.

USES AND ECONOMICS. Ammonia is the most important nitrogenous material. Most is made synthetically but some continues to be obtained as by-product. Chilean saltpeter ($NaNO_3$) continues to be mined and is a significant source of fixed nitrogen. Ammonia gas is used directly as a fertilizer, in heat treating, paper pulping, nitric acid and nitrates manufacture, nitric acid ester and nitro compound manufacture, explosives of various types, and as a refrigerant. Urea, hydroxylamine, and hydrazine are made from it. Amines, amides, and miscellaneous other organic compounds are derived from ammonia. Use of ammonia as a fertilizer is very great but remains far below that desirable for maximum crop production. Thirteen

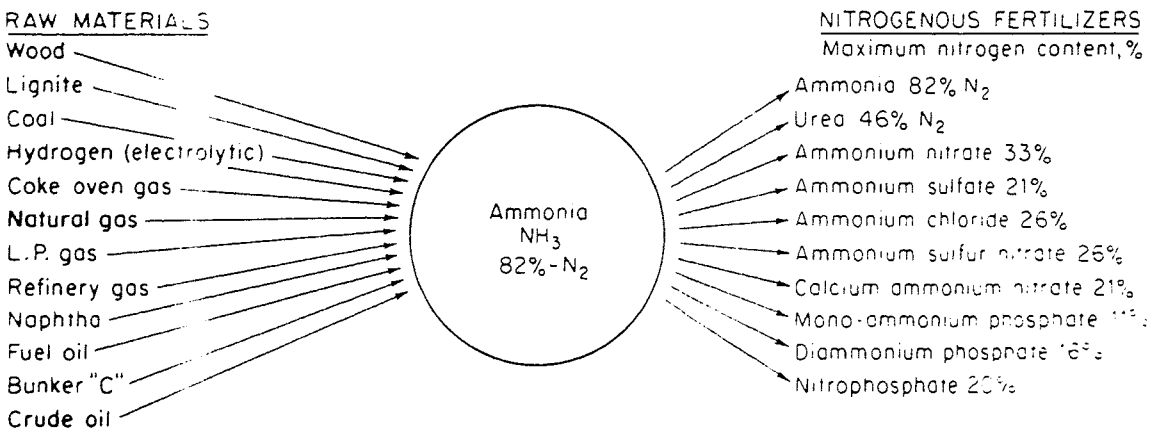

Fig. 3.1. Raw materials used throughout the world to manufacture ammonia and nitrogenous fertilizers produced from ammonia. In the United States, 95 percent of the hydrogen required is based on natural gas or other hydrocarbons. [*Chem. Eng. Prog.* 49 (11) 63 (1963).]

countries use over 200 kg/ha of mixed fertilizers ($N + P_2O_5 + K_2O$), many others well below 25 kg/ha. Presumably all countries could profit by more extensive use.

RAW MATERIALS. Air, water, hydrocarbons, and power are the usual materials used. Coal can replace the hydrocarbons, but the process is more complex and expensive. See Fig. 3.1.

SYNTHETIC AMMONIA

USES AND ECONOMICS. Ammonia is a major raw material for industry and agriculture as shown in Table 3.1. The total tonnage consumed in the United States exceeded 19×10^6 t in 1981.[1] Nitric acid production uses 20 percent of production, urea 20 percent, and ammonium phosphates 15 percent. The uses are 80 percent in fertilizers, 20 percent in plastics and fibers, and 5 percent in commercial and military explosives. Commercial grades include essentially pure liquid NH_3 and aqueous ammonia, usually standardized at 28% NH_3. Cylinders and tank cars move much material, but pipelines over 1000 km long extend from production to distribution centers. Table 3.2 shows the major nitrogen-containing compounds produced in the U.S.

REACTIONS AND EQUILIBRIUMS. For the reaction

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g) \qquad \Delta H_{12°C} = -46.0 \text{ kJ} \qquad \Delta H_{659°C} = -55.6 \text{ kJ} \qquad (1)$$

an equilibrium constant can be expressed as

$$K_p = \frac{p_{NH_3}}{p_{N_2}^{1/2} \times p_{H_2}^{3/2}}$$

Because the product molecule, ammonia, has a lower volume than the reactant molecules, the equilibrium yield of ammonia is increased by increasing pressure (Fig. 3.2). Temperature increase produces the opposite effect on the equilibrium, but increases the rate of reac-

[1] t = 1000 kg.

Table 3.1 Ammonia and Ammonia Compounds Produced in the United States (in thousands of metric tons of contained nitrogen)

Compound	1970	1975	1976	1979	1980	1981
Ammonia, synthetic	10,335	12,353	12,492	13,924	14,686	14,225
Ammonium compounds, coking plants						
Ammonia liquor	11	11	4	6	6	na*
Ammonium sulfate	115	118	101	87	75	na
Ammonium phosphates	8	8	na	na	na	na
Total	10,469	12,490	12,597	14,017	14,767	14,225

*na = not available.

SOURCE: *Minerals Yearbook 1981*, Dept. of the Interior, 1982.

NOTES: 14,255,000 t of contained nitrogen = 17,310,000 t of 100% ammonia. At the last available census, there were 40 producers of ammonia in the United States, some with several plants, many shut down. The largest plant has a capacity of 1500 t/day.

tion greatly. This negative temperature effect on equilibrium combined with a strong positive effect on rate is common to many other reactions and requires a nice balance of conditions to assure good operating conditions and to make profits possible. Greater rate means reduced equipment size and consequent equipment cost.

RATE AND CATALYSIS OF THE REACTION. To keep equipment size small, the rate of the reaction must be increased substantially, since hydrogen and nitrogen alone react together extremely slowly. Commercial syntheses require an efficient catalyst to increase reaction rate to an acceptable figure. Ammonia catalysts of several types have been tested, but plants now use iron with added promoters—oxides of aluminum, zirconium, or silicon at about 3% concentration and potassium oxide at about 1%. These prevent sintering and make the catalyst more porous. For a given rate of gas flow, if pure iron produces 3 to 5 percent conversion, singly promoted iron can produce 8 to 9 percent and doubly promoted iron 13 to 14 percent. New catalysts are claiming concentrations near 25%. Iron catalysts lose their activity rapidly if heated above 520°C. Catalysts are also deactivated by contact with copper, phosphorus, arsenic, sulfur, and carbon monoxide, which alter the iron composition. This causes much trouble and expense in purifying the gases for the reaction. Chapter 6 discusses the purification of synthesis gases. Catalysts sufficiently robust to withstand higher levels of impurities and effective at lower temperatures (permitting higher equilibrium conversions) would be most valuable.

The exact mechanism by which the catalyst functions is not entirely clear, but certainly

Table 3.2 Major Nitrogen-Containing Compounds Produced in the United States (in thousands of metric tons)

Compound	1972	1975	1978	1979	1980	1981
Acrylonitrile	506	636	796	917	832	912
Ammonium nitrate	6255	6955	6,555	7,539	8,297	7,992
Ammonium sulfate	2246	2545	2,636	2,253	2,033	1,919
Ammonium phosphates	5908	6727	10,470	10,984	12,162	11,037
Nitric acid	7255	7545	7,213	8,105	8,392	8,218
Urea	3191	3445	5,703	6,364	7,118	6,918

SOURCE: *Minerals Yearbook 1981*, Dept. of the Interior, 1982.

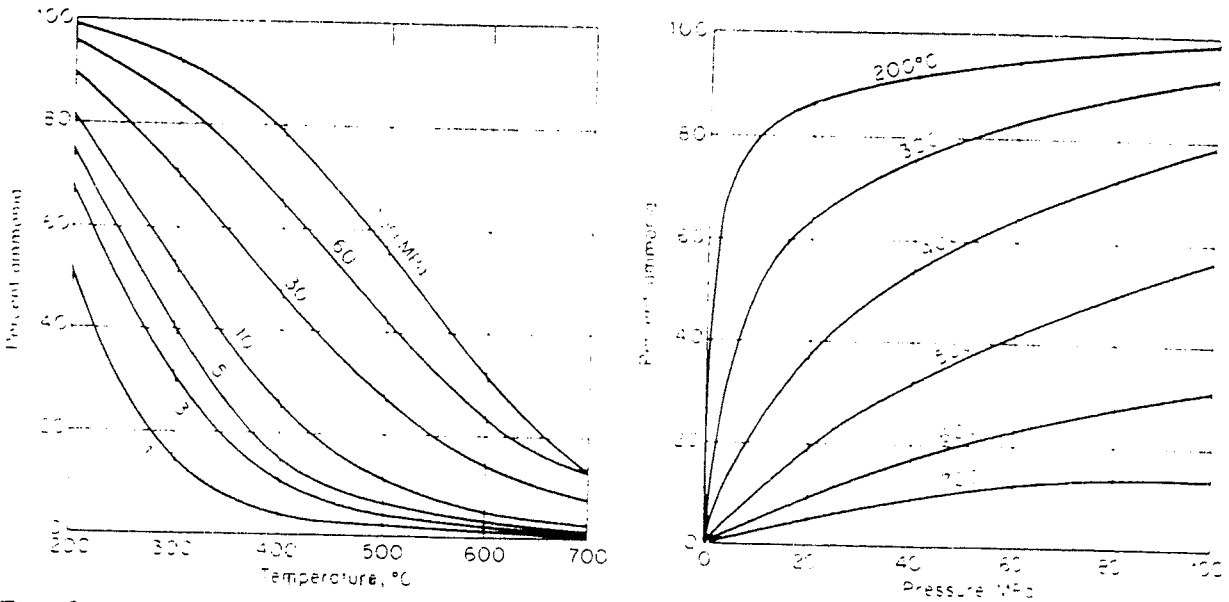

Fig. 3.2. Percentage of ammonia at equilibrium from an initial mixture of 3:1 H_2 N_2 gas at various temperatures and pressures. *(Comings, High Pressure Technology, p. 410. Compare Frear and Baber, ECT, 2d ed., vol. 2, 1963, p. 260.)*

the N and H either react chemically with the surface or are adsorbed, then migrate, probably forming H, N, NH, NH_2, and NH_3 in that order, followed by desorption.

Space velocity is the volume of gases, corrected to standard conditions (0°C and 101 kPa) that pass over one volume of catalyst per unit time. Of course, the percentage of ammonia produced at a given temperature and pressure and for a given catalyst decreases with increasing space velocity. Different commercial plants have varying space velocities, reflecting the differences in catalysts and reactors. Most industrial units use a space velocity between 10,000 and 20,000 per hour.

MANUFACTURING PROCEDURES. Manufacturing consists essentially of six phases (see Fig. 3.3): (1) manufacture of reactant gases, (2) purification, (3) compression, (4) catalytic reaction, (5) recovery of ammonia formed, and (6) recirculation. Cost is greatly influenced by the pressure, temperature, catalyst, and raw materials used. Of most current interest is heat recovery and reuse. Different groups have developed procedures satisfactory for their local

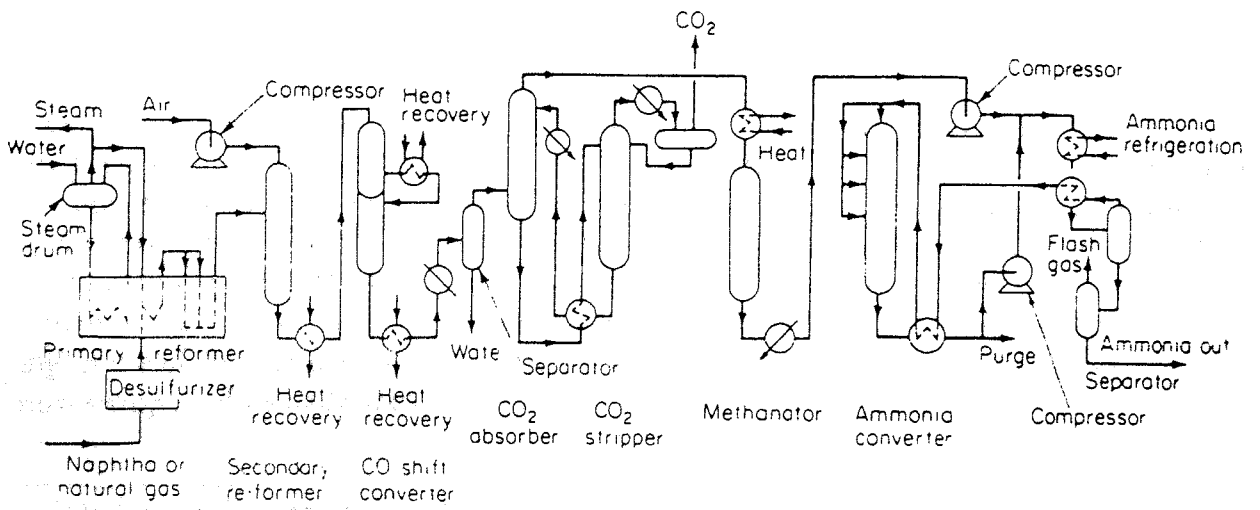

Fig. 3.3. The Kellogg ammonia process. *(M. W. Kellogg Co.)*

conditions. The elimination of intermediate storages, single train construction, and the use of rotary (replacing reciprocating) compressors have made the capacity of today's plants much larger (up to 1650 t/day) than those of yesterday. The greatly increased cost of energy has made them more complex because of the need to conserve energy. In 1950, 55.9 GJ/t were required to make ammonia, this has been reduced to 26 in 1982 and continues to fall. Many plants produce steam for outside use while requiring little power as input. These factors and extreme worldwide competition have kept ammonia prices low.

There is as much difference in the economical sources of hydrogen as any variable. The principal hydrogen-manufacturing process in the United States in 1982 was a combination process in which natural gas, air, and steam were reacted with the addition of heat over a catalyst to produce a 3:1 mixture of hydrogen and nitrogen along with carbon dioxide and water. The carbon dioxide and water were then removed. Synthesis gas production is detailed in Chap. 6. Other systems used in some areas are: electrolysis of water (a pressure process is being developed[1a] that may be competitive soon), by-product hydrogen, cracking of hydrocarbons, coal-water and hydrocarbon-water interactions, and partial oxidation of hydrocarbons. There are also many totally untried (commercially) ideas being put forward.

SYNTHESIS SYSTEMS. All ammonia syntheses are based on the overall reaction (1) shown earlier. This reaction is quite exothermic, so the design of the converter (Fig. 3.4) must protect the unit from overheating, both to ensure control at the optimum temperature for conversion and to protect the shell against metallurgical deterioration at the high pressure and temperature. The flowchart of Fig. 3.3 illustrates the basic steps of a current system.

Ammonia synthesis gas is prepared by high-pressure catalytic reforming of hydrocarbon feed, usually natural gas freed of sulfur, in the presence of steam over a nickel catalyst in the primary reformer, then subjected to a catalytic "shift" at a lower temperature in the presence of air in one or more secondary reformers. The shift reaction serves two purposes—(1) it produces more hydrogen per unit of fuel, and (2) it oxidizes much of the carbon monoxide to the more easily removed carbon dioxide. It has become customary to add an oversize charge to the low-temperature-shift catalyst bed. This "guard" catalyst captures sulfur and chlorine poisons and extends the main catalyst's life over 100 percent. After CO_2 removal by water and then chemical absorption, any residual CO and CO_2 is completely converted to methane in the methanator. Methane is an inert gas with respect to the ammonia catalyst. Throughout the entire process, conservation and reuse of heat is so vital that it has been said that an ammonia plant is really a steam generating plant that incidentally produces ammonia. Much more steam than ammonia is made (4:1).

After catalytic methanation at about 2.75 MPa, the 3:1 hydrogen-nitrogen mixture, freed of carbon-containing compounds except for a little methane, is raised to the full reaction pressure of about 20 MPa by means of a (usually) turbine-driven centrifugal compressor. Various methods of temperature regulation are used in the converters: heat exchange coils are inserted or cold gas injected between beds. The ammonia is then recovered by means of refrigeration or absorption and handled as an anhydrous liquid under modest pressure.

After the ammonia is removed, the remaining gases are far too valuable to discard. They contain all the inerts fed to the system (CH_4, Ar, Ne, etc.) at the highest concentration anywhere in the system. The concentration of inerts is, therefore, regulated by removing (purging) some of this gas continuously. When fuel was quite cheap, this gas was burned, but it is now stripped of its undesirables and reused.

[1a]daRosa, A Compressorless Ammonia Process, *CHEMTECH* 118 (1) 28 (1978).

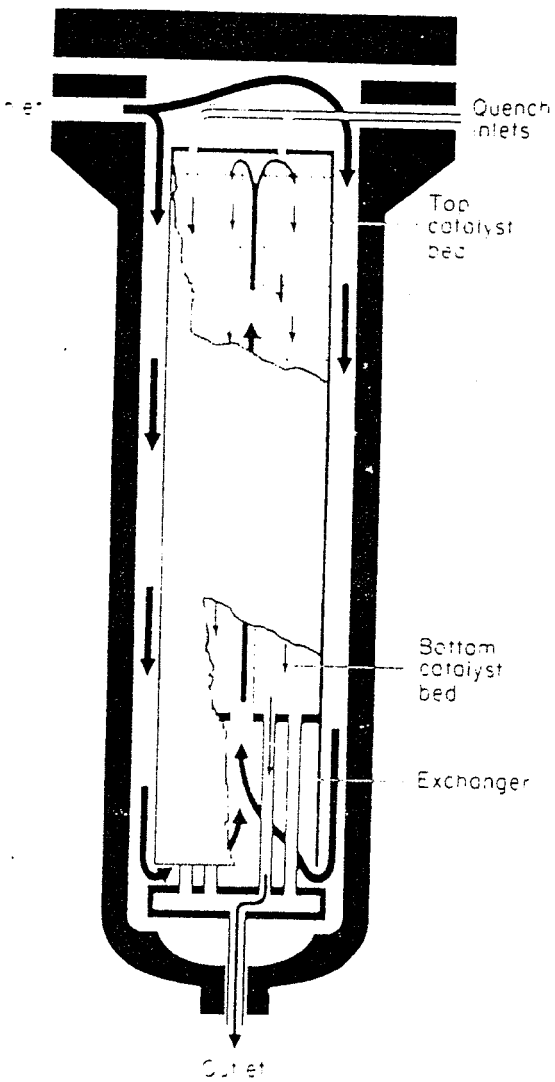

Fig. 3.4. Ammonia-synthesis converter. The converter consists of a high-pressure shell containing a catalyst section and a heat exchanger. The catalyst section is a cylindrical shell which fits inside the pressure shell, leaving an annular space between the two. The catalyst section contains several beds supported on screened grids. To maintain the catalyst at optimum temperature for maximum yield, cold feed-gas quench is injected before each catalyst bed. The top bed contains the smallest quantity of catalyst. Since the temperature gradient is flatter in succeeding beds, bed sizes are graduated, with the largest bed at the bottom. Beneath the catalyst section is the heat exchanger. This preheats fresh inlet gas against hot reacted gas from the last catalyst bed. The top quench point permits the introduction of feed gas without preheating and provides temperature control to the first catalyst bed.

The feed gas enters at the top of the converter and flows downward between the pressure shell and the wall of the catalyst section. The gas cools the shell and is heated. The gas then enters the exchanger at the bottom of the converter and, by circulating around the exchanger tubes, is further preheated against hot effluent. Some feed gas is introduced directly to the top of the first bed, where it meets the preheated feed. The combined stream at a temperature of 370 to 425°C is then introduced into the top catalyst bed. The gas passes downward through the catalyst, with a rapid temperature rise as the ammonia reaction proceeds, and then through the catalyst supporting grid into a space between the first and second beds. Here the temperature is reduced and the ammonia content diluted by injection of cold feed gas. This permits control throughout the catalyst beds to obtain optimum temperatures for maximum yields. In a like manner, the gas flows downward through the lower catalyst beds. (*M. W. Kellogg Co.*)

In the 1970s, a revolution in ammonia manufacturing came about as the reciprocating compressors common at that time were replaced by centrifugal units. At that time, the ammonia process was regarded as highly efficient, a mature process, but careful examination of the process step-by-step and the severe economic pressure led to major improvements and cost drops approaching 50 percent. Some of the important changes made are summarized below.

1. When operating procedures were carefully studied, it became possible to operate without duplication of equipment (single train) and to eliminate intermediate storage.

2. Quality catalysts made it possible to operate economically at the lower pressures at which centrifugal compressors are most economical. Higher pressures were used when only reciprocating units were available.

3. Large capacity compressors, better catalysts, and better converters made larger units attractive and permitted many economies that were a result of the larger size.

4. By raising the temperature of the primary reformer outlet and preheating the air to the endothermic secondary reformer, manufacturers reduced the overall cost of reforming. Primary re-formers operate at very high temperatures, so they are far more expensive than secondary ones. Shift reactors are now commonly two-stage.

5. Digital computer control of process variables has narrowed the range of variation and given consistently better operation at nearer to maximum conditions.

6. Most carbon dioxide is removed by absorption in water, but the final stripping requires the use of an alkaline reagent. Three processes compete: (a) inorganic absorbents (usually K_2CO_3), (b) organics (mainly amines), and (c) "physical" absorbents (Fluor's propylene carbonate). The choice is made based on residual CO_2 level, effect of impurities, and problems of regeneration.

7. Bleed gas from the synthesis loop, formerly burned, is now recovered with substantial reduction (near 15 percent) in energy requirement per unit of product. Cryogenic separation (Petrocarbon Co.) recovers hydrogen and some nitrogen. Gaseous diffusion[2] through hollow fibers (Monsanto's Prism) recovers hydrogen only. With the Prism process the two separated streams are, typically, 89% hydrogen, 6% nitrogen, 5% inerts and 20% hydrogen, 42% nitrogen, and 38% inerts. It is also possible to separate inerts, usually by scrubbing with nitrogen, before gas enters the synthesis loop (Braun); this makes possible a much smaller purge. A completely different approach uses a pressure swing molecular sieve system after the high-temperature shift reaction to produce a highly purified hydrogen feed. This eliminates the secondary reformer and no air is added to the system, so nitrogen must be obtained by air distillation or some similar process.

8. Synthesis converters are now highly developed and vastly improved over previous designs. Both horizontal and vertical types are used with cooling by quenching, a common practice, but some cooling with tubular inserts is also done.[3] Inlet gases conventionally pass along the shell, being preheated and reducing the maximum shell temperature. Low pressure drop is desirable to reduce operating costs; small catalyst size reduces required catalyst volume (high area-to-volume ratio). Most conversion occurs in the first bed, for there the driving force toward equilibrium is greatest. Designs of axial and radial flow converters from 500 to 1600 t/day are available. Modern designs use pressures of 15 to 30 MPa at around 500°C. Outlet concentrations of ammonia are 16 to 25%.

9. Low-cost ammonia recovery from converter outlet gases has several options. Multiple-stage refrigeration combined with some reduction in pressure is usually used. If cooling water is very cold, some water condensing may be possible. Where markets are nearby, a water wash to produce aqua ammonia may be desirable. Excess steam may be used to run an absorption refrigeration system to condense the ammonia. The problem is one of cost.

COST. The method of production of the hydrogen and the feedstock selected are the major items influencing the final cost of the ammonia produced. Much effort is currently being exerted to reduce costs by reducing steam and fuel requirements. Presently operating plants use 40 to 45 GJ per metric ton of ammonia produced. With simplified processing procedures, improved catalysts, and operation at pressures low enough to permit a one-stage compressor,

[2]Ricci, Tightening the Loop in Ammonia Manufacture, *Chem. Eng.* 86 (3) 54 (1979).

[3]Forster, Improved Reactor Design for Ammonia Synthesis, *Chem. Eng.* 87 (18) 62 (1980).

energy use can theoretically be reduced to 21 GJ per metric ton. Plants designed to produce ammonia at 27 GJ per metric ton are currently available, but the current unfavorable economic conditions have prevented construction of such plants and reduced the retrofitting of improvements.

AMMONIUM NITRATE

Ammonium nitrate is a very important nitrogenous fertilizer because of its high nitrogen content (33%), the simplicity and cheapness of its manufacture, and its valuable combination of quick-acting nitrate and slower-acting ammoniacal nitrogen. Its tendency to cake on storage reduced its acceptability at first but proper granulation, the addition of antihygroscopic agents, and better packaging have largely remedied this problem. Most commercial and many military explosives contain cheap ammonium nitrate as the major explosive ingredient. Ammonium nitrate is difficult to detonate, but, when sensitized with oil or mixed with other explosive materials, it can be detonated with a large booster-primer. Ammonium nitrate mixtures are "permissibles," that is, permitted for use in coal mines where combustible vapors may be encountered. The use of explosives in mines and quarries provides a large and continuing market. Amatol is a mixture of TNT and granular ammonium nitrate (AN). This is the major conventional military explosive. On explosive decomposition, AN rapidly and violently decomposes to form elemental nitrogen.

$$NH_4NO_3 \rightarrow 2N_2 + 4H_2O + O_2$$

Under different conditions, i.e., at 200 to 260°C, it is safely decomposed to form the anaesthetic nitrous oxide. This is the commercial method of preparation.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

Ammonium nitrate is made by reacting nitric acid (made by oxidizing ammonia) with ammonia:

$$NH_3(g) + HNO_3(aq) \rightarrow NH_4NO_3(aq) \qquad \Delta H = -86.2 \text{ kJ}$$

If properly proportioned and preheated, the reaction can be run continuously to produce molten ammonium nitrate containing very little water (1 to 5%) which can be formed into small spheres (prills) by dropping the reaction product through a shot tower or into flakes by cooling it on belts or drums. By fluidized bed treatment, it is possible to obtain a dry granular material as product. Batch processes have also been used, but the labor and equipment costs are prohibitive. Figure 18.5 shows a typical flowchart.

AMMONIUM SULFATE

Ammonium sulfate, which has little tendency to cake on storage, was accepted by farmers long before ammonium nitrate was made noncaking. Originally it was made by using sulfuric

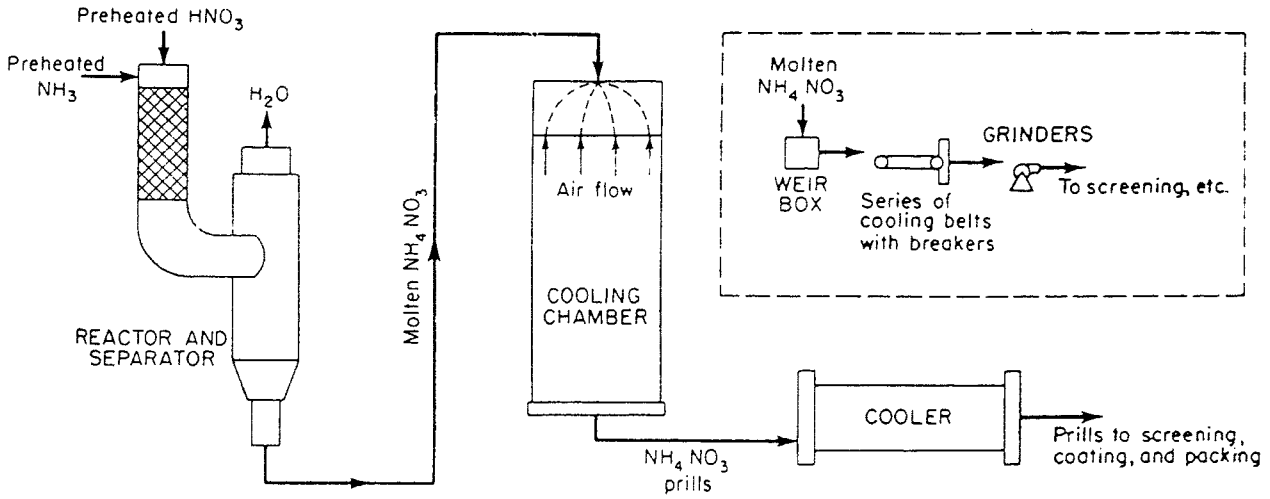

Fig. 3.5. Simplified flowchart for the Stengel process for ammonium nitrate manufacture. *(Commercial Solvents Corp. and L. A. Stengel.)*

acid to scrub by-product ammonia from coke-oven gas, and much is still produced in this manner. However, most ammonium sulfate is now made by reaction between synthetic ammonia and sulfuric acid. Production is about 2.3×10^6 t/year with about 20 percent from by-product ammonia. Where sulfur for sulfuric acid is at a premium, for example at Sindri, India, a process based on gypsum and carbon dioxide from combustion is used:

$$(NH_4)_2CO_3(aq) + CaSO_4 \cdot 2H_2O(s) \rightarrow CaCO_3(s) + 2H_2O + (NH_4)_2SO_4(aq)$$

Anhydrite can also be used. Some ammonium sulfate is also obtained as a by-product of caprolactam (for nylon-6) manufacture.

AMMONIUM PHOSPHATES

There are three possible ammonium orthophosphates, only two of which are manufactured on any scale. Monoammonium phosphate (MAP) is readily made by reacting ammonia with phosphoric acid, centrifuging, and drying in a rotary dryer. It is used in quick-dissolving fertilizers and as a fire-retarding agent for wood, paper, and cloth. Diammonium phosphate (DAP) requires a two-stage reactor system in order to prevent loss of ammonia. A granulation process follows with completion of the reaction in a rotary drum.

UREA

Urea is in many ways the most convenient form for fixed nitrogen. It has the highest nitrogen content available in a solid fertilizer (46%). It is easy to produce as prills or granules and easily transported in bulk or bags with no explosive hazard. It dissolves readily in water. It leaves no salt residue after use on crops and can often be used for foliar feeding. In addition to fertilizer use, it is used as a protein food supplement for ruminants, in melamine produc-

tion, as an ingredient in the manufacture of resins, plastics, adhesives, coatings, textile antishrink agents, and ion-exchange resins. It is an intermediate in the manufacture of ammonium sulfamate, sulfamic acid, and pthalocyanines. Annual production in the United States is very large, 6.4×10^6 t at \$150 to \$160 per metric ton in 1982.

Two reactions are involved in the manufacture of urea. First, ammonium carbamate is formed under pressure by reaction between carbon dioxide and ammonia

$$CO_2 + 2NH_3 \xrightarrow[180°C]{14\ MPa} NH_2COONH_4 \qquad \Delta H = -155\ MJ/kg \cdot mol$$

This highly exothermic reaction is followed by an endothermic decomposition of the ammonium carbamate

$$NH_2COONH_4 \rightleftharpoons NH_2CONH_2 + H_2O \qquad \Delta H = +42\ MJ/kg \cdot mol$$

Both are equilibrium reactions. The formation reaction goes to virtual completion under usual reaction conditions; the decomposition reaction is less complete. Unconverted carbon dioxide and ammonia, along with undecomposed carbamate, must be recovered and reused. This is a troublesome step. The synthesis is further complicated by the formation of a dimer called biuret, $NH_2CONHCONH_2 \cdot H_2O$, which must be kept low because it adversely affects the growth of some plants.

Once-through operation was once practiced with the unchanged ammonia converted to ammonium compounds, but this is now too expensive, and the markets for the secondary products are problematical. Partial and total recycle plants have been built, but only total recycle plants are considered now.

The conventional plant decomposes the carbamate in one or more decomposers, each at a lower pressure than the previous one. All evolved gases must be repressured to the reactor pressure, and this is expensive. Presently the most popular method is designed to minimize the use of energy by "stripping" the product liquor by contacting it with incoming carbon dioxide and by using some of the heat of formation of carbamate to bring about the endothermic decomposition and the rest to generate process steam. Figure 3-6 shows a flowchart for the process. Liquid ammonia, gaseous carbon dioxide, and recycle materials meet in a heat exchanger–reactor at a pressure of 14 MPa at 170 to 190°C to form carbamate with most of the heat of reaction carried away as useful process steam. The carbamate decomposition reaction is both slow and endothermic. The mix of unreacted reagents and carbamate flows to the decomposer. The stoichiometric ratio of CO_2/NH_3 conversion to urea is essentially about 55 percent, but by using an excess of CO_2 (or NH_3), the equilibrium can be driven as high as 85 percent. The reactor must be heated to force the reaction to proceed. The flowchart shows a decomposer followed by a stripper in which CO_2 is introduced; these are at substantially identical pressures, requiring no gas recompression—only a small liquid recycle pump. For all the unreacted gases and undecomposed carbamate to be removed from the product, the urea must be heated at lower pressure (400 kPa). The reagents are reacted and pumped back into the system. Evaporation and prilling or granulating produce the final product. Overall, over 99 percent of both CO_2 and NH_3 are converted to urea, making environmental problems minimal. Carbamate is highly corrosive to both ordinary and stainless steels, but with oxygen present, 300 series stainless steels resist it very well, so some air is introduced along with the CO_2 reagent to reduce system corrosion.

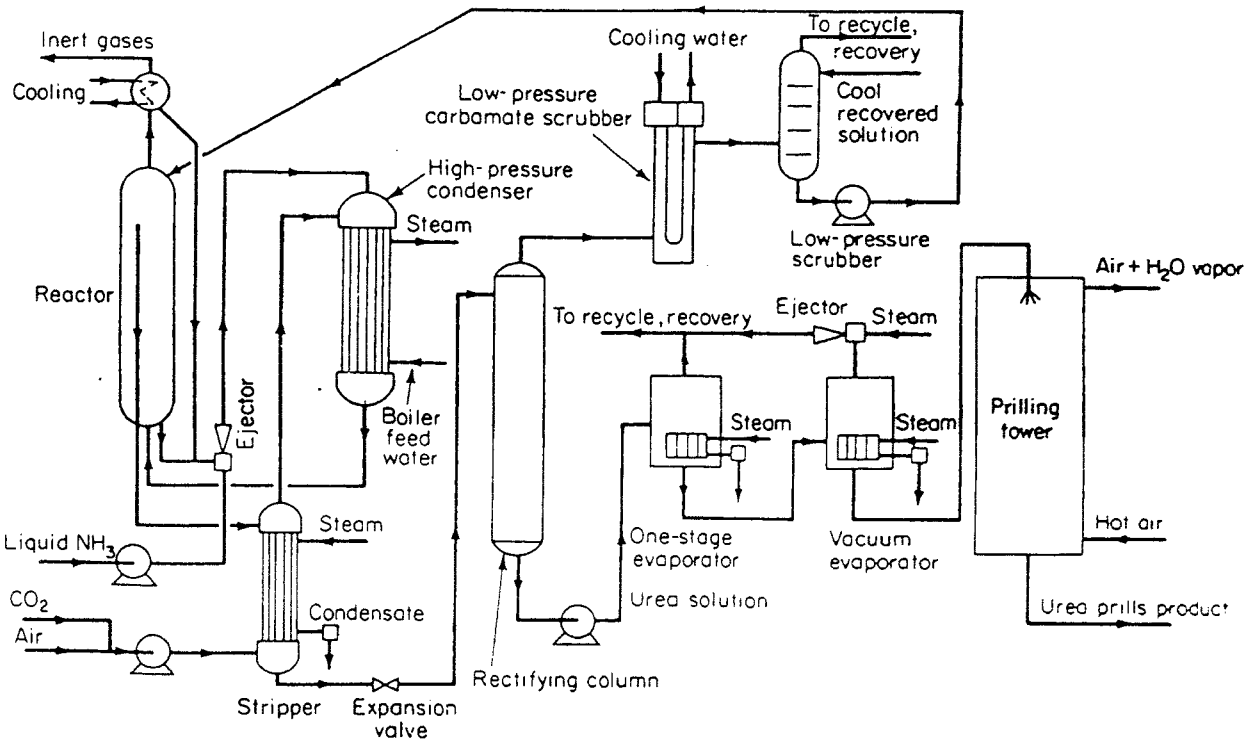

Fig. 3.6. Simplified flow chart, Stamicarbon urea stripping process. *(Stamicarbon and M. W. Kellogg Co.)*

NITRIC ACID

HISTORICAL. Nitric acid has been known and esteemed for a long time. Distillation of saltpeter with sulfuric acid is the usual ancient method of preparation. Lightning forms considerable amounts in the atmosphere.

Ammonia can be burned in air in the presence of a platinum catalyst, and the nitrogen oxides thus formed can be oxidized further and absorbed in water to form nitric acid. Cheap ammonia has made this process much less expensive than the older synthesis from Chilean saltpeter.

USES AND ECONOMICS. Most nitric acid is used in making ammonium nitrate. The manufacture of other organic and inorganic nitrates along with organic nitro compounds uses substantial quantities. Sodium, copper, and silver nitrates are produced on a large scale. Direct applications include photoengraving, metal pickling and passivating, and the parting of gold and silver.

Phosphate rock for fertilizer use has its phosphorus made available for plant use by acidulation with sulfuric acid. Acidulation with nitric acid adds desirable nitrogen fertilizer to the phosphorus already present. Nitric acidulated fertilizer cakes on storage, but this difficulty is gradually being overcome; this market is potentially large.

Organic nitrates (nitroglycerine, glycol nitrate, cellulose nitrates) and nitro compounds (TNT, RDX, picric acid) all require nitric acid for their synthesis. Nitroparaffins are also made on a large scale by vapor phase nitration with nitric acid. Nitric acid's strong oxidizing characteristics in dilute solutions, usually highly objectionable in organic syntheses, are sometimes most useful.

Commercial grades are made to specification, usually from 36 to 42°Bé (53.4 to 68.7% w/w). Highly concentrated acid (94.5 to 95.5%) known to the trade as "concentrated" acid is made in specially designed plants and is more expensive. It can be made from weaker acid by extractive distillation with strong dehydrating agents such as sulfuric acid and magnesium sulfate.

RAW MATERIALS. Ammonia, air, water, and platinum-10% rhodium gauze catalyst are the essential materials. Location near an ammonia plant is usually desirable. Since it requires only 17 kg of ammonia to contain 1 kg-atom of nitrogen, but 105 kg of 60% nitric acid, it may be cheaper for large users to ship ammonia rather than nitric acid. Stainless-steel cars and trucks handle nitric acid solutions.

REACTIONS AND ENERGY CHANGES. The following reactions have been observed as of major importance in nitric acid manufacture:

	ΔH, kJ/kg·mol	
(overall) $NH_3(g) + 2O_2(g) \rightarrow HNO_3(aq) + H_2O(l)$	−437	(1)
$4NH_3(g) + 5O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g)$	−227	(2)
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	−57.1	(3)
$3NO_2(g) + H_2O(l) \rightleftharpoons 2HNO_3(l) + NO(g)$	−58.7°	(4)
$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$	−317	(5)
$4NH_3(g) + 6NO(g) \rightarrow 5N_2(g) + 6H_2O(g)$	−451	(6)
$2NO_2(g) \rightarrow N_2O_4(g)$	−28.7	(7)

Varies with HNO_3 concentration.

Gaseous mixtures of oxides of nitrogen (NO, N_2O_3, NO_2, N_2O_4) are commonly referred to as NOX regardless of composition.

Manufactured acid contains some nitrous acid (HNO_2) when the concentration is between 20 and 45% HNO_3 w/w and dissolved N_2O_4 when the concentration is over 55%. The oxidation potential of 20 to 45% acid stabilizes trivalent nitrogen (HNO_2), over 55% stabilizes tetravalent nitrogen (N_2O_4).

Reaction (2) is a swift (when catalyzed) reaction, complete in less than a millisecond. It must, therefore, be run as an adiabatic reaction. The concentration of ammonia feed must be limited so that the maximum temperature reached does not damage sive catalyst.

Reaction (3) is a slow, gas-phase reaction with third-order kinetics and a rate that with increasing temperature. Complete conversion to NO_2 is not commercially p

Reaction (4) shows several troublesome features despite its fair speed and the re ΔH. Approach to equilibrium is reasonably rapid, but the equilibriur If the acid is too concentrated or too hot, the reverse reaction occurs equilibrium for reaction (4) as a plot of log $(p_{NO}/p^3_{NO_2})$ in the gas pha in the liquid phase with temperature as a parameter. The absorption re complicated than (4) indicates, for NO_2, N_2O_3, N_2O_4, and HNO_2 are all

[4]Theobald, Messungen zum Gleichgewicht Saltpetersauren/Nitrose Gase, *Chem. Ing. Tech.* **40** (15) 763 (1968).

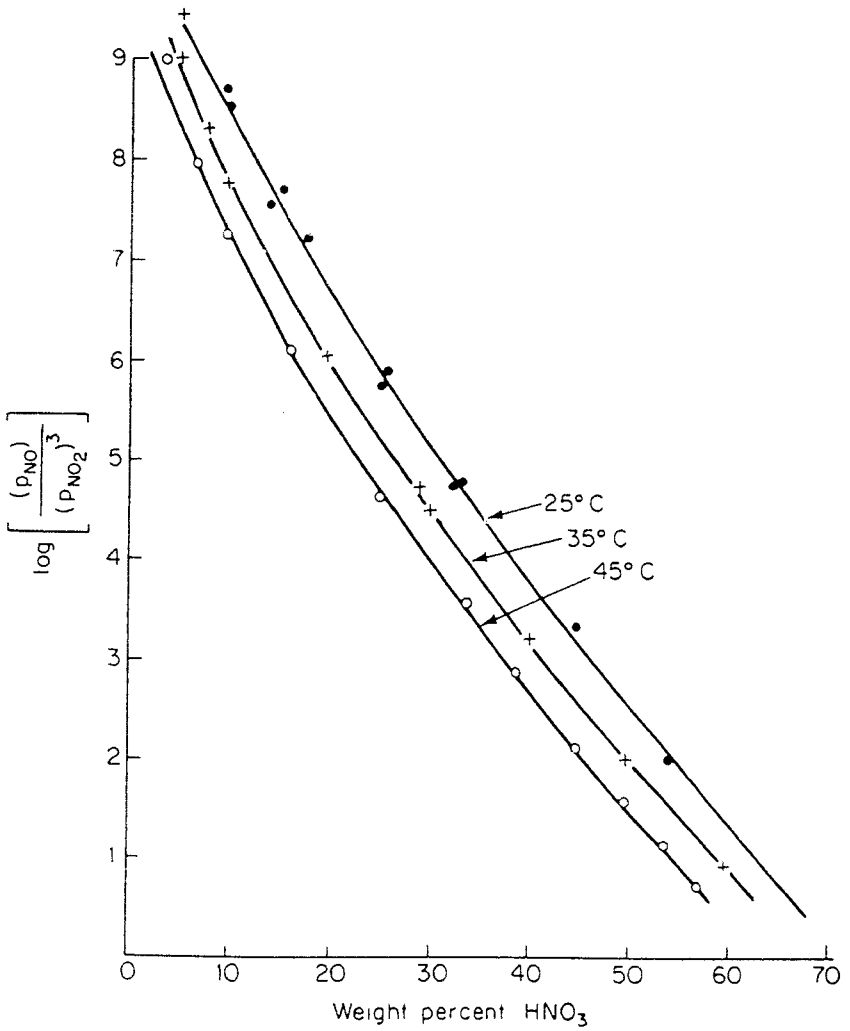

Fig. 3.7. An equilibrium constant for nitric acid manufacture.

to produce HNO_3, but one-third of all such dissolved gases are then expelled as NO, requiring reoxidation and reabsorption until the quantity of NO remaining is very small. This is a time-consuming process.

MANUFACTURING PROCEDURES. Originally the whole oxidation-absorption-reoxidation-reabsorption process operated at atmospheric pressure. Such plants are expensive because the equipment is large. Atmospheric pressure plants cannot produce acid stronger than 50 to 55% HNO_3. Such plants are not now being considered.

Two types of units dominate current production—single-pressure plants (commonly known as American or DuPont) and dual-pressure systems (called European). The single-pressure plant has lower capital cost and produces more by-product steam; the dual-pressure unit has a lower catalyst cost and a slightly higher yield. Currently, overall costs are almost exactly competitive.[5]

The Single-Pressure Process. The single-pressure process is shown in the flowchart of Fig. 3.8. A multiple-stage rotary compressor with intercoolers between stages is driven by a

[5]Harvin, Leray, and Roudier, "Single Pressure or Dual-Pressure Nitric Acid—An Objective Comparison," AIChE 71st Annual Meeting Preprint, 1978.

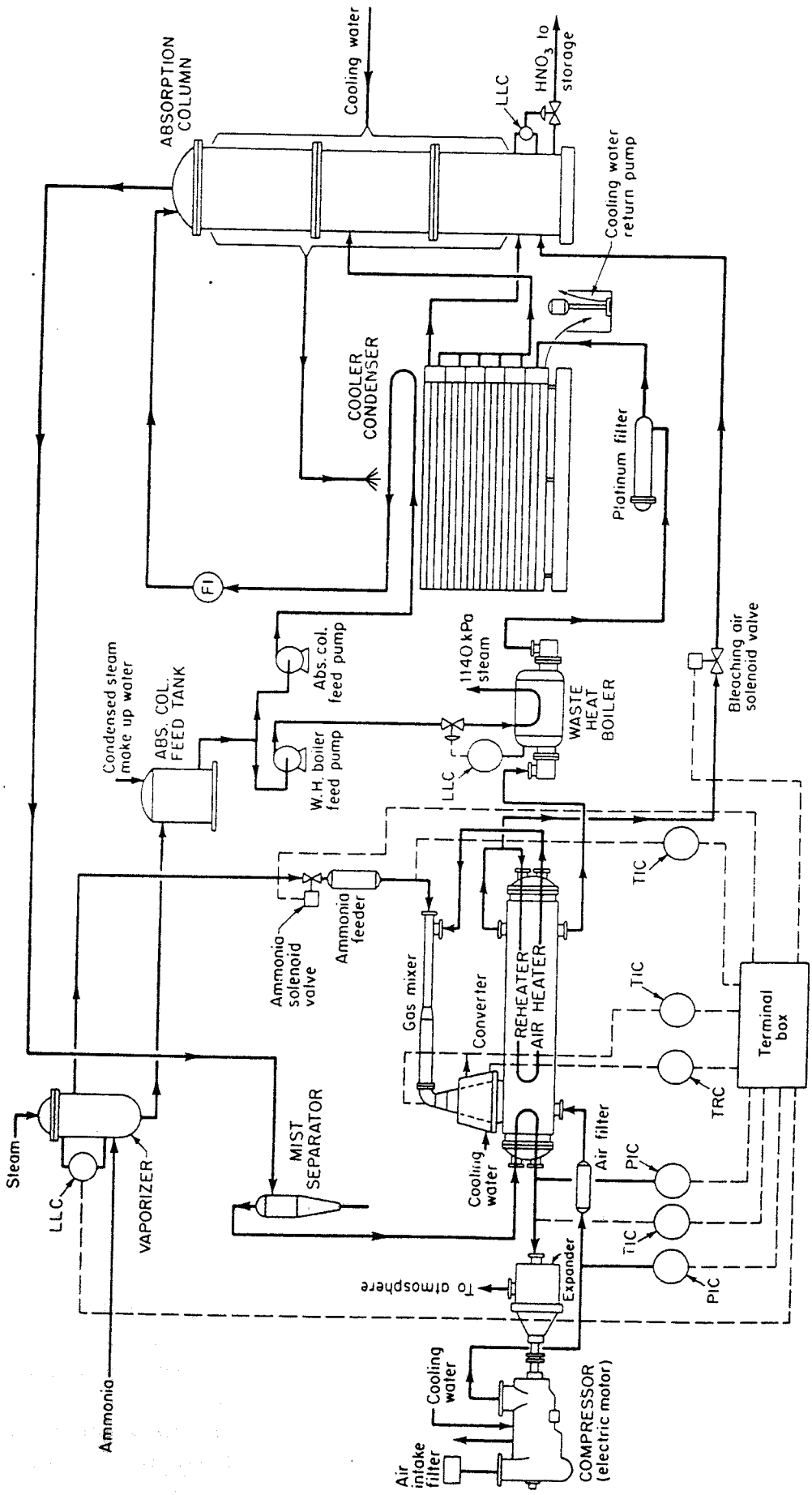

Fig. 3.8. Flowchart for the manufacture of 60% nitric acid from ammonia: DuPont high-pressure (10 MPa) self-sustaining 225-t/day unit. The expander turbine operates on the heat of the tail gas (essentially N_2). A high-efficiency platinum filter collects platinum volatilized or eroded and is essential to economic operation. LLC, liquid level controller; FI, feed intake; LIC, liquid level indicating controller; PIC, pressure indicating controller; TIC, temperature indicating controller; TRC, temperature recording controller. *(E. A. Rass, Chemical and Industrial Co.)*

steam turbine and a power recovery turbine, the so-called "tail-gas expander." Stage intercooling is regulated to give an outlet temperature near 230°C at 1 MPa.

The outlet air is split, 85 percent going to the converter and 15 percent to heat exchangers and the bleach column. The hot compressed air is mixed with superheated ammonia and sent to the converter, which operates at 800 to 950 kPa. The air-ammonia mix, containing about 10% ammonia, passes through a stack of about 30 layers of 80 mesh platinum + 10% rhodium gauze. Combustion is rapid, with an exit temperature of 940°C. The conversion to NO is 94 to 95 percent and about 62 g of platinum alloy is required per metric ton of daily acid capacity. Gas temperature and ammonia concentration to the reactor are critical. Above 11.5 to 12% ammonia, explosion is possible. The entering gas must be at least 205°C, preferably 230°C, for the first layer of gauze to remain at reaction temperature, but the gauze temperature must not exceed 940°C or catalyst loss will be excessive. At 10% ammonia, the adiabatic temperature rise is 710°C, thus restricting the ammonia concentration to 10%. Catalyst life is 6 to 10 weeks, largely as a result of erosion. This causes a catalyst charge of approximately $5 per metric ton of 100% HNO_3 produced. Cobalt trioxide–containing pellets are also being used and require less frequent replacement, but conversion is somewhat lower.

Converter exit gas is passed through a steam superheater, a waste heat boiler, and a tail gas preheater, emerging at about 200°C. It then passes into a cooler-condenser which produces 40 to 45% HNO_3 as product containing about 40% of the fixed nitrogen. Both cooled exit gas and dilute nitric acid pass on to the absorber, still under full pressure of 980 kPa. The absorber-reactor is a sieve plate or bubble cap unit with cooling coils on each of the 20 to 50 trays. Gas enters at the bottom, dilute nitric acid part way up the column, with cold water entering at the top. The temperature of the exit gas is near 10°C. Two pinch points caused by kinetic problems occur within the column. Near the bottom, the rate of reoxidation of evolved NO is slow because the strong acid present prevents rapid absorption of NO_2 causing slow evolution of NO. Near the top, the concentrations of NOX and oxygen become so low that the driving force for absorption is small.

The acid leaving the bottom of the column contains some NOX, mostly as N_2O_4 (colorless) but some as red NO_2. This is "bleached" by passing it through a column countercurrent to the 15% primary air (needed for oxidation of NO to NO_2) bled off from the air compressor. Some plants include the bleach section at the bottom of the main absorber column.

Chlorine impurity presents a unique problem in the absorber. Chlorides cannot leave through the bottom because the strong nitric acid oxidizes them to chlorine, which is swept up the column. They cannot leave in the top gas because here NO reduces them to HCl which goes down the column in the aqueous phase. The combination of HCl and HNO_3 is highly corrosive. Chlorides must, therefore be excluded from entry or provision made for their purging.

Air pollution problems are created because it is too expensive to try to absorb more than 97 to 98 percent of the NO leaving the gauze. U.S. federal air pollution regulations require 99.8 percent absorption. Three methods are currently used to meet requirements. (1) Stack gas is reheated to 680°C and reacted with natural gas. The combustion reaction between natural gas and NO increases the gas temperature and this increases the power recovered in the expander. (2) Reheated stack gas can be treated with ammonia or hydrogen (if available from a nearby ammonia plant) in a catalytic reactor to reduce the NO to N_2. The temperature rise is quite small. (3) Additional absorption capacity operating at low temperature (e.g., 5°C) can increase absorption sufficiently to meet requirements. The equipment will be very large, for the driving force for absorption will be quite small.

The Dual-Pressure Process. The dual-pressure process buys lower catalyst cost by using lower velocities, larger diameter catalyst beds with thinner gauze layers (only four), and oper-

ates with lower pressure, 240 kPa, in the converter. Gases then pass through heat recovery systems and are compressed to 990 kPa for absorption and bleaching. The rest of the process is similar to the single-pressure process.

The dual-pressure system reduces catalyst cost sharply to about $1.50 per metric ton of 100% HNO_3 produced. It requires about 2 percent less power but recovers about 5 percent less power and produces less by-product steam compared with the single-pressure system. The weight of catalyst per unit of daily production is about the same for both processes.

Both processes give highly efficient production of the same quality product and yield effluent gases within the same pollution potential limits.

SODIUM NITRATE

Sodium nitrate has both fertilizer and industrial uses: fluxes, fireworks, pickling, heat-treating mixes, tobacco additive. In the highlands of Chile, great natural deposits occur, some 8 to 65 km wide and 0.3 to 1.2 m thick under a shallow overburden. Simple countercurrent leaching and crystallization produces a good quality product. For years these deposits dominated the world's fixed nitrogen supply. Much of the world's iodine is obtained as a by-product of $NaNO_3$ production. With lowered ammonia cost, reactions between salt or soda ash and nitric acid meet current needs at modest prices. Some plants respond more favorably to $NaNO_3$ than to competing nitrogen sources.

POTASSIUM NITRATE

Potassium nitrate is manufactured in two ways: (1) by reacting nitric acid with potassium chloride with a chlorine by-product, and (2) reacting sodium nitrate with potassium chloride and crystallizing out the salt. It is an excellent fertilizer with two useful fertilizing components—13% N, 44% K_2O. Other uses include explosives, ceramics, and heat-treating salts.

CYANAMIDE

At one time cyanamide was a useful agricultural fertilizer; later its major importance came from it derivative—dicyandiamide. Its use has now sharply diminished until only one small plant remains. Its production is of considerable historical interest because a large plant was built to produce it at the end of World War I, but it was never successful commercially. Earlier editions of this book give details of its production.

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Chapter 4

Sulfur and Sulfuric Acid

Sulfur is one of the most important and basic materials in the chemical process industries. It exists in nature both in the free state and combined in ores such as pyrite (FeS_2), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$). It is also an important constituent of petroleum and natural gas (as H_2S). The largest application of sulfur is in the manufacture of sulfuric acid.[1]

HISTORICAL. Sulfur has a history as old as any other chemical and has developed from the mystic yellow of the alchemist to one of the most useful substances in modern civilization. It was burned in early pagan rites to drive away evil spirits, and even then the fumes were used as a bleach for cloth and straw. For many years, a French company held a monopoly on sulfur by controlling the world supply from Sicily. Partly because of monopolistic high prices and partly because of the abundance of pyrites, elemental sulfur was little used in the United States prior to 1914. Though sulfur was discovered in the U.S. Gulf of Mexico region in 1869, it was difficult to mine because of overlying beds of quicksand. Before 1914, the United States made most of its sulfuric acid from imported and domestic pyrite and from by-product sulfur dioxide from copper and zinc smelters. The mining of sulfur in Texas and Louisiana by the Frasch process was increased, starting around 1914, to such an extent that it provided for most domestic needs and entered world markets. In recent years a major source of elemental sulfur is H_2S, which is a by-product of the desulfurization of sour (i.e. sulfur-containing) natural gas and sour crude oil. Canada, France, and the United States are the largest producers of recovered sulfur.

In 1980, world production of sulfur in all forms amounted to 54.6×10^6 t,[1a] of which 26.1 percent was Frasch-produced, 32.2 percent recovered, 5.5 percent other elemental, and 36.2 percent obtained from nonelemental sources such as pyrites and smelter gases.

USES AND ECONOMICS. The United States produced 13×10^6 t of elemental sulfur in 1981. Of this, 48.8 percent was by the Frasch hot water process, 17.7 percent from oil refineries, and 15.4 percent by desulfurization of natural gas. Net imports were 1.13×10^6 t. Frasch production, which in 1982 represented 53 percent of the U.S. supply, is predicted to fall to 29 percent by 1990 as the amount of recovered sulfur continues to increase. Other sources expected to be of future importance are: shale oil, coal gasification, synthetic fuel projects,

[1]Duecker and West, *Manufacture of Sulfuric Acid*, ACS Monograph No. 144, Reinhold, New York, 1959 (most important for both sulfur and sulfuric acid, many references); *Sulfur and SO_2 Developments*, Chemical Engineering Progress Technical Manual, 1971.

[1a]t = 1000 kg.

and gypsum[2] (or anhydrite). World stockpiles of sulfur exceed 26×10^6 t with Saudi Arabia, Poland, and Iraq likely to increase the oversupply as new sulfur supplies are tapped there.

Over 90 percent of the sulfur used is converted to sulfuric acid, but other industrial uses abound. Some of these are: in the manufacture of wood pulp, carbon disulfide, insecticides, fungicides, bleaching agents, vulcanized rubber, detergents, pharmaceuticals, and dyestuffs. Among some new uses being studied are: (a) as an extender for paving asphalt, (b) sulfur concretes and mortars, (c) plant and soil treatment, (d) sulfur-alkali metal batteries, and e foamed sulfur insulation.[3]

MINING AND MANUFACTURE OF SULFUR

Elemental sulfur ores were mined manually before the development of the Frasch process. The sulfur in these ores was then concentrated by burning part of the sulfur in piles to melt the remainder, drawing off the liquid, and casting it into molds. The development of the Frasch process made such mining impossibly expensive. Native sulfur deposits are mechanically mined in Eastern bloc countries, and to a lesser extent in other countries. Marketable sulfur is produced by heating in autoclaves, drawing off the liquid, and casting it into large blocks from which it is subsequently reclaimed as a solid. Some is converted to flowers of sulfur by distillation (sublimation).

Ores (from volcanic and similar deposits), without upgrading, can be roasted (burned) to make sulfur dioxide gas, which is used to produce sulfuric acid and for other purposes. Elemental sulfur is also produced by removing hydrogen sulfide from natural and refinery gases with absorbents such as mono- and/or diethanolamines. The hydrogen sulfide is then converted to elemental sulfur by the Claus or modified Claus process. This process is described under sulfur from fuel gases.

FRASCH PROCESS. The major tonnage of all the elemental sulfur of the world has been obtained from the sulfur-bearing porous limestones of the saltdome caprocks of Texas, Louisiana, and Mexico by the Frasch process. As early as the late 1890s, Herman Frasch devised his ingenious method[4] of melting the sulfur underground or under the sea and then pumping it up to the surface. Ordinary oil-well equipment is used to bore holes to the bottom of the sulfur-bearing strata, a distance underground from 150 to 750 m. A nest of three concentric pipes, varying in size from 3 to 20 cm in diameter, passes through the sulfur-bearing stratum and rests on the upper portion of the barren anhydrite, as shown in Fig. 4.1. A 10-cm pipe passed through the 20-cm one so that an annular space exists between the two, extends nearly to the bottom of the sulfur-bearing rock, and rests on a collar that seals the annular space between the 20- and the 10-cm pipes. An air pipe, 3 cm in diameter, inside the others, reaches to a depth slightly above the collar mentioned above. The 20-cm pipe is perforated at two different levels, one above and the other below the annular collar. The upper set of perfora-

[2]Higson, $CaSO_4$ as a Raw Material for Chemical Manufacture, *Chem. Eng. News* 29 (43) 4469 (1951); Hill, Schonand, and Zergiebal, *Ind. Eng. Chem.* 49 (8) 1204 (1957).

[3]Davis, Sulfur: New Uses Needed, *Chem. Eng.* 79 (17) 30 (1972).

[4]Sulfur Mining at Newgulf, *Chem. Eng.* 48 (3) 104 (1941); Haynes, *The Stone that Burns*, Van Nostrand, New York, 1970.

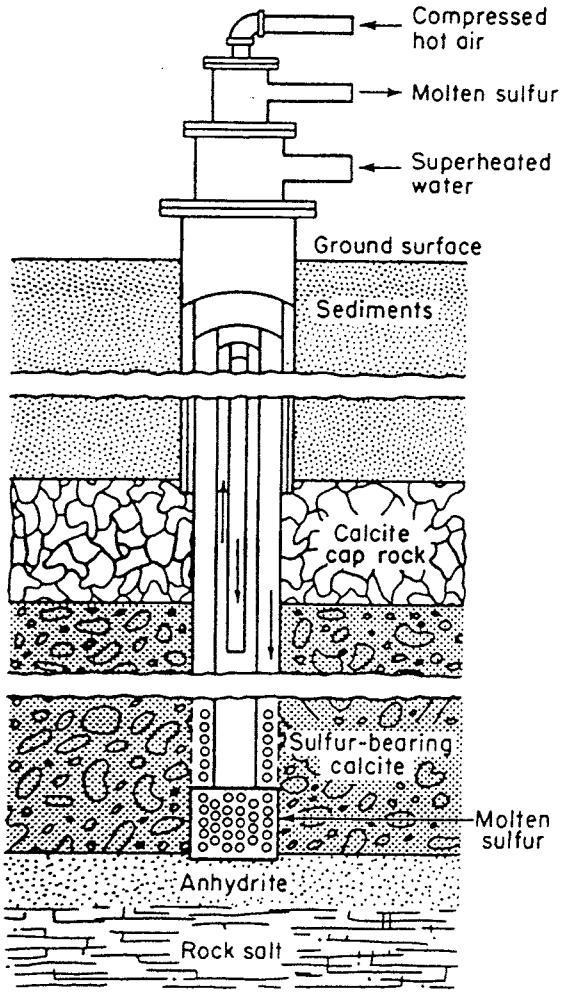

Fig. 4.1. Schematic diagram of the Frasch process for mining sulfur. *(McGraw-Hill Encyclopedia of Science and Technology.)*

tions permits escape of the hot water, and molten sulfur enters the system through the lower perforations.

For operation of the well, hot water at about 160°C is passed down the annular space between the 20- and the 10-cm pipes. It discharges through the perforations into the porous formation near the foot of the well. The sulfur-bearing rock around the well through which this water circulates is raised to a temperature above the melting point of sulfur, about 115°C. Molten sulfur, being heavier than water, sinks and forms a pool around the base of the well, where it enters through the lower perforations and rises in the space between the 10- and the 3-cm pipes. The height to which the sulfur is forced by the pressure of the hot water is about halfway to the surface. Compressed air forced down the 3-cm pipe aerates and reduces the density of the liquid sulfur so that it will rise to the surface. The compressed air volume is regulated so that the production rate is equalized with the sulfur melting rate in order not to deplete the sulfur pool and cause the well to produce water. Water must be withdrawn from the formation at approximately the same rate as it is injected to prevent a buildup of pressure to the point where further injection would be impossible. Bleed wells for extracting water from the formation usually are located on the deeper flanks of the dome to withdraw the heavier cold water which accumulates there. Water heating capacities of existing power plants are as high as 38,000 t/day. The amount of water required to produce 1 t of sulfur depends on the richness of the deposit and other factors. Requirements may range from 4 to 50 t per metric ton of sulfur mined.

On the surface, the liquid sulfur moves through steam-heated lines to a separator where

the air is removed. The sulfur can be either solidified in large storage vats or kept liquid in steam-heated storage tanks. More than 95 percent of all U.S. sulfur is shipped as a liquid in insulated tank cars, tank trucks, and heated barges or ships. This reduces freight costs and gives the purchaser much purer sulfur.

SULFUR FROM FUEL GASES. Increasingly hydrogen sulfide is being removed[5] during the purification of sour natural gas, coke-oven gas, and from petroleum refinery gas by dissolving it in potassium carbonate solution or ethanolamine, followed by heating to regenerate it (see Chap. 6). The hydrogen sulfide thus produced is burned to give sulfur dioxide for sulfuric acid. However, the majority is converted to elemental sulfur by various modifications of the original Claus process, for which the reactions are:

$$H_2S(g) + \tfrac{3}{2}O_2(g) \rightarrow SO_2(g) + H_2O(g) \qquad \Delta H = -518.8 \text{ kJ} \qquad (1)$$

$$SO_2(g) + 2H_2S(g) \xrightarrow{Fe_2O_3} 3S(l) + H_2O(g) \qquad \Delta H = -142.8 \text{ kJ} \qquad (2)$$

The use of this process is illustrated in the flowchart of Fig. 19.2. Air pollution regulations require new plants to attain over 98 percent conversion, and the province of Alberta, Canada, is asking for 99.5 percent conversion.[6] To meet the new emission regulations, a number of processes have been developed for cleaning the residual sulfur values from the tail gases of recovery plants.[7] A process used to treat the tail gases is shown in Fig. 4 .2. Approximately one-half of the world production of elemental sulfur is made by gas treatment.

Other existing or potential sources of sulfur include coke-oven gases and synthetic crude oils from tar sands or shale oil. Tar sands and shale oil plants are being operated in Canada and Brazil.[8] Very little sulfur is presently recovered from coal, but efforts to reduce sulfur dioxide emissions by developing clean fuels from coal could produce significant amounts in the future. Coal cleaning technology can remove about half of the sulfur in coal, but the organic sulfur can be removed only by gasification, liquefaction, and hydrogenation processes. Several such processes are in various stages of development.[9] Where sulfur-containing

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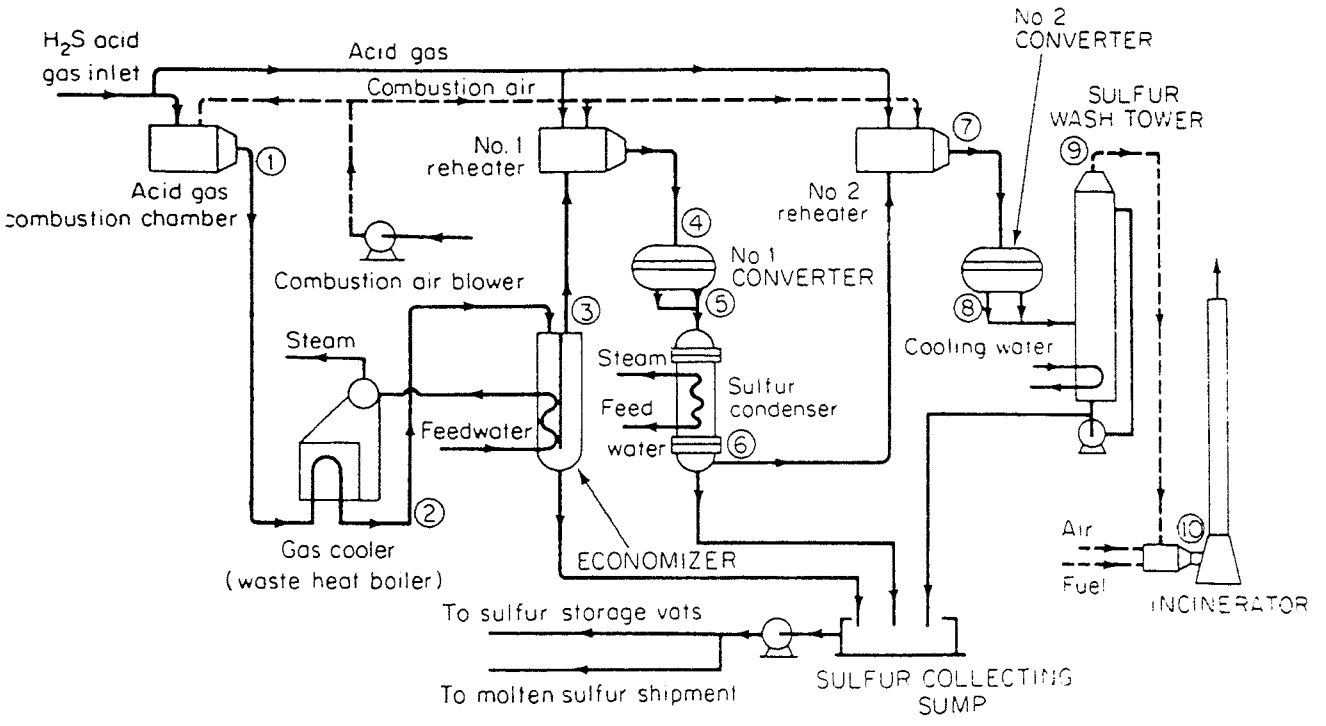
[5]Brennan, Amine Treating of Sour Gas: Good Riddance to H_2S, *Chem. Eng.* 69 (22) 94 (1962); Heppenstall and Lowrison, The Manufacture of Sulfuric Acid, *Trans. Inst. Chem. Eng.* 31 389 (1953); Sulfur from H_2S, *Chem. Eng.* 59 (10) 210 (1952); Duecker and West, op. cit. chaps. 4, 5, and 9; Estep, McBride, and West, *Advances in Petroleum Chemistry and Refining*, vol. VI, chap. 7, Interscience, New York, 1962.

[6]Rowland, *Oil Week*, Oct. 23, 1974, p. 9.

[7]Aquitane Cleans Claus Tail Gas with Sulfreen Unit, *Oil Gas J.* 70 (26) 85 (1972); Davis, Add-on Process Stems H_2S, *Chem. Eng.* 79 (11) 66 (1972); Barry, Reduce Claus Sulfur Emission, *Hydrocarbon Process.* 51 (4) 102 (1972); Chalmers, Citrate Process Ideal for Claus Tail-gas Cleanup, *Hydrocarbon Process.* 53 (4) 75 (1974); Ludberg, "Removal of Hydrogen Sulfide from Coke Oven Gas by the Stretford Process," paper presented at the 64th annual meeting of the Air Pollution Control Association, Atlantic City, N.J., 1971.

[8]Pattison, Oil Begins to Flow from Canadian Tar Sands, *Chem. Eng.* 74 (24) 66 (1967); Franco, Brazil Tries New Shale Oil Process, *Oil Gas J.* 70 (37) 105 (1972).

[9]Chopey, Taking Coal's Sulfur Out, *Chem. Eng.* 79 (16) 86 (1972); *Environ. Sci. Technol.* 8 (6) 510 (1974).



The acid gas feed (191,000 std m^3/day, 38°C) is composed of 75.1% H_2S, 24.7% CO_2, and 0.2% hydrocarbons. *(Monsanto Enviro-Chem.)*

Location	Temperature, C°	Location	Temperature, C°
1	1049	6	166
2	379	7	208
3	149	8	224
4	258	9	133
5	332	10	538

Fig. 4.2. Claus-type sulfur recovery unit of the Okotoks plant.

fuels have to be burned, sulfur oxides must be removed by stack gas cleaning methods, or by new combustion techniques designed to remove sulfur during burning.[10]

SULFUR FROM OTHER SOURCES. Because of stringent air pollution regulations, sulfuric acid plants are being installed to remove and utilize SO_2 in gases resulting from the roasting of sulfide ores, smelting of ores, and burning of spent acid or acid sludge from petroleum refining. Liquid sulfur dioxide is occasionally the preferred product from these sources.

Conventional copper smelters have limited sulfur recovery capability because certain portions of the off gas are too low in sulfur dioxide concentration to make sulfuric acid economically. Electrical furnaces and flash smelters produce more concentrated sulfur dioxide suitable for the recovery of elemental sulfur or sulfuric acid.[11]

[10]Slack, *Sulfur Dioxide Removal From Waste Gases*, Noyes, Park Ridge, N.J., 1971; ER&E Sets Pilot Plant to Burn High-Sulfur Coal with Low SO_2 Discharge, *Oil Gas J.* 70 (47) 83 (1972).

[11]Semrau, Sulfur Oxides Control and Metallurgical Technology, *J. Met.* 23 (3) 41 (1971); White, SO_2 Laws Force U.S. Copper Smelters into Industrial Russian Roulette, *Eng. Min. J.* 172 (7) 61 (1971).

Several commercial processes for recovering elemental sulfur from pyrite ores include the Outokumpu flash-smelter process, the Orkla process, and the Noranda process. Only the Outokumpu process is still being used commercially. The Outokumpu flash smelter, as well as the Mitsubishi and Noranda continuous smelters, are also being used for continuous smelting of copper ores and delivering high-strength sulfur dioxide gases for sulfuric acid manufacture.

Today, pyrite and zinc sulfide ores are usually roasted in fluidized[12] bed roasters although a few flash roasters and multiple hearth roasters still exist. Acid sludges from petroleum refining are being successfully regenerated[13] to produce clean recycled sulfuric acid. The recovery of sulfur from stack gases in power stations has not materialized except for a few small installations. Power plants, when required to treat their stacks, usually treat the gases with alkaline solutions of lime or sodium and discard the residue, usually calcium sulfate and/or sulfite.

Sulfur derived from pyrite roaster and smelter off gases amounted to almost 20×10^6 t worldwide in 1980.

SULFURIC ACID

It is difficult to believe that a very active chemical such as sulfuric acid is at the same time one of the most widely used and most important technical products. It is the agent for sulfate formation and for sulfonation, but more frequently it is used because it is a rather strong and cheaply priced inorganic acid. It enters into many industries, though infrequently appearing in the finished material. It is employed in the manufacture of fertilizers, leather, and tin plate, in the refining of petroleum, and in the dyeing of fabrics.

HISTORICAL.[14] The origin of the first sulfuric acid is unknown, but it was mentioned as far back as the tenth century. Its preparation, by burning sulfur with saltpeter, was first described by Valentinus in the fifteenth century. In 1746, Roebuck of Birmingham, England, introduced the lead chamber process. This interesting, but now obsolete process is described in detail in the third edition of this book and elsewhere.[15]

The contact process was first discovered in 1831 by Phillips, an Englishman, whose patent included the essential features of the modern contact process, namely, the passing of a mixture of sulfur dioxide and air over a catalyst, followed by the absorption of the sulfur trioxide in 98.5 to 99% sulfuric aicd. Phillips' invention was not a commercial success for more than 40 years, probably because (1) there was a lack of demand for strong acid, (2) inadequate knowledge of catalytic gas reactions, and (3) the slow progress of chemical technology. Development of the dye industry resulted in a rising demand for concentrated acids for the manufacture of alizarin and other organic coloring matter. In 1889, it was demonstrated that an excess of oxygen in the gaseous mixture for the contact process was advantageous. The contact

[12]Fluidized Bed Technique Pays Off in New Sulfuric Acid Plant, *Chem. Eng.* 62 (8) 288 (1955); Guccione, From Pyrite: Iron Ore and Sulfur, *Chem. Eng.* 73 (4) 122 (1966); Hester, Johannsen, and Danz, Fluidized Bed Roasting Ovens, *Ind. Eng. Chem.* 50 1500 (1958).

[13]Sander and Daradimos, Regenerating Spent Acid, *Chem. Eng. Prog.* 74 (9) 57 (1978); Duecker and West, op. cit., chap. 18.

[14]Duecker and West, op. cit., Fairlie, *Manufacture of Sulfuric Acid*, Reinhold, New York, 1936. Both are standard reference books with bibliographies and sketches.

[15]Faith, Keyes, and Clark, *Industrial Chemicals*, 4th ed., Wiley-Interscience, New York, 1975; Fairlie, op. cit.

process has been improved in all details and is now one of industry's low-cost, automatically controlled, continuous processes[16] (see Fig. 4 .4). All the new sulfuric acid plants use the contact process. One of the disadvantages which led to the demise of the chamber process is that it can produce acid of only 78% strength. Concentration is expensive, thus by 1980, only one chamber plant was still in operation in the United States.

PROPERTIES OF SULFURIC ACID. Sulfuric acid is a strong dibasic acid. In addition, it is also an oxidizing and dehydrating agent, particularly toward organic compounds. Its dehydrating action is important in absorbing water formed in such chemical conversions as nitration, sulfonation, and esterification, thus ensuring high yields.

Solutions of sulfuric acid may be concentrated economically to about 93% by weight of H_2SO_4. Stronger acids may be made by dissolving sulfur trioxide in 98 to 99% acid. Sulfuric acid forms many hydrates that have fairly definite melting points, as shown in Table 4.1. The irregularities in the relation between strengths of the sulfuric acids and the corresponding specific gravities and freezing points are due to these hydrates.

Sulfuric acid is widely sold in the form of various solutions of H_2SO_4 in water, or of SO_3 in H_2SO_4. The latter, called oleums, are marketed on the basis of the percentage of SO_3 present; 20% oleum means that, in 100 kg, there are 20 kg of SO_3 and 80 kg of H_2SO_4. This 20% oleum, if diluted with water to make 100% acid (monohydrate), would furnish 104.5 kg total weight. Previously, when much of the acid was made by the chamber process, solutions of sulfuric acid in water were sold according to their specific gravity or their Baumé (Bé°) degrees. Table 4.2 illustrates the standard sulfuric acids of commerce. For sulfuric acid the usual temperature to which specific gravity, or Baumé degrees, are referred is 15°C. The specific gravity of sulfuric acid increases gradually to 1.844 at 15°C for 97% acid, after which it decreases to 1.839 at 15°C for 100% acid. Consequently, in this upper range, i.e., above 95%, the strengths must be determined by means other than density. For some of the medium-range oleums, however, density is again helpful. Electrical conductance, refractive index, and sonic transmittance are being used to measure continuously acid strength in modern plants.

As contact plant acid has displaced chamber plant acid, the H_2SO_4 percentage is now normally specified. Acid containing 93.19% H_2SO_4 (66°Bé acid) is the normal acid of commerce in North America. This acid is cheap to transport as it has little water and can be stored and shipped in steel tanks and containers. Its freezing point (−7°C) is lower than that of 96% acid. Acid of somewhat higher strength (about 95% H_2SO_4) is normally used in Europe. Lesser

[16]For a listing of sulfuric acid plants in the United States, see *Chem. Mark. Rep.* May 7, 1979.

Table 4.1 Hydrates of Sulfuric Acid

	Formula	Melting Point, °C	Specific Gravity
Sulfuric, acid, fuming	$H_2S_2O_7$	35	$1.9^{20°}$
100%	H_2SO_4	10.37	$1.834^{18°/4}$
Monohydrate	$H_2SO_4 \cdot H_2O$	8.48	$1.842^{15°/4}$
Dihydrate	$H_2SO_4 \cdot 2H_2O$	−38.57	$1.650^{0°/4}$

SOURCE: Rubin and Giaque, The Heat Capacities and Entropies of Sulfuric Acid and Its Mono- and Dihydrates from 15 to 300 K. *J. Am. Chem. Soc.* 74 800 (1952).

***Table* 4.2** Commercial Strengths of Sulfuric Acid

	Degrees Bé. 15.6°C	Specific Gravity, 15.6°C	Sulfuric Acid, %
Battery acid	29.0	1.250	33.33
Chamber acid, fertilizer acid, 50° acid	50	1.526	62.18
Glover or tower acid, 60° acid	60	1.706	77.67
Oil of vitriol (OV), concentrated acid 66° acid	66	1.835	93.19
98% acid		1.841	98.0
100% H_2SO_4		1.835	100.0
20% oleum,* 104.5% acid		1.915	104.5
40% oleum, 109% acid		1.983	109.0
66% oleum		1.992	114.6

*For oleums, percent means free SO_3.

SOURCE: Duecker and West, *Manufacture of Sulfuric Acid*, ACS Monograph 144, Reinhold, New York, 1959, pp. 2 and 411 (modified).

quantities of 98% acid and oleum are shipped. Acid of 93% H_2SO_4 strength is completely suitable for fertilizer manufacture, which is the major use for sulfuric acid.

The normal strengths of commercial oleums fall into three categories, expressed as percent free sulfur trioxide: 10 to 35%, 40%, and 60 to 65%. The freezing point of 35% oleum is about 29°C, and of 40% oleum about 34°C; consequently, small amounts of nitric acid are sometimes added (where this is tolerable) to these grades to inhibit freezing during winter shipment.

PRODUCTION AND USAGE. Fertilizer manufacture, as shown in Table 19.3, is the greatest single use of sulfuric acid. When superphosphate was the usual phosphatic fertilizer, the chamber process sulfuric acid plant and the superphosphate plant were built and operated at the same site. These were small plants located near farming areas.

More concentrated fertilizers are now required in order to reduce the costs of transportation and application. Plants for triple superphosphate are more capital intensive than ordinary superphosphate plants. They are built on a much larger scale, and, like previous superphosphate plants, operate at the same site as the contact plant. The product acid has a strength of

***Table* 4.3** Major U.S. Markets for Sulfuric Acid (million metric tons 100% H_2SO_4 and percentage)

	1979	%	1980	%
Phosphate fertilizer	23.2	60.9	26.0	64.5
Petroleum refinery	2.4	6.3	2.6	6.5
Chemicals	2.3	6.0	2.0	5.0
Ore processing	2.5	6.6	2.0	5.0
Pulp and paper products	0.8	2.1	0.7	1.7
Paints and pigments	0.6	1.6	0.7	1.7
Nitrogen fertilizer	0.5	1.3	0.7	1.7
Steel pickling	0.9	2.4	0.3	0.7
All other	4.9	12.8	5.3	13.2
Total	38.1	100.0	40.3	100.0

SOURCE: *End Uses of Sulfur and Sulfuric Acid in 1980*; Mineral Industry Surveys, U. S. Bureau of Mines, May 27, 1981.

93.2% H_2SO_4, which can be safely stored in steel tanks. It is diluted as part of the phosphate-producing facility if lower strength is desired.

When chamber plants supplied acid, several different grades were supplied, each with a particular use. Grades of 53 to 56°Bé were employed in superphosphate manufacture, so the chamber plants could supply this acid without expensive concentration. Battery acid is even more dilute. The 60°Bé grade was used in the manufacture of sulfates of ammonia, copper (bluestone), aluminum (alums), magnesium (Epsom salts), zinc, iron (copperas), etc., and organic acids such as citric, oxalic, acetic, and tartaric; and for pickling iron and steel before galvanizing and tinning, refining and producing heavy metals, electroplating, and preparing sugar, starch, and syrup. Strong sulfuric acid, 93 to 99%, is utilized in the purification of petroleum products, preparation of titanium dioxide, alkylation of isobutane, manufacture of many nitrogen chemicals, synthesis of phenol, recovery of fatty acids in soap manufacture, and manufacture of phosphoric acid and triple superphosphate. Oleums are needed for petroleum, nitrocellulose, nitroglycerin, TNT, and dye manufacture as well as for fortifying weaker acids. There are many other uses; in fact, few chemical products are manufactured without the use of sulfuric acid.

Free world production capacity for sulfuric acid for 1979 and 1980 is shown in Table 19.4. This shows that the 1980 installed free world capacity is 431,000 t/day, equivalent to about 155×10^6 t/year. U.S. capacity in 1980 was 153,000 t/day, equivalent to approximately 50×10^6 t/year.

U.S. usage was 40.3×10^6 t for 1980, indicating that plants in the United States were then producing at about 80% of capacity.

Manufacture

When the sole problem involved was forming H_2SO_4 at a reasonable concentration from SO_2 generated by burning sulfur or pyrites and when energy was cheap, plants were relatively uncomplicated. When energy prices increased sharply, the high-level energy resulting from the oxidation of sulfur and sulfur dioxide became a valuable commodity. Major changes in plant design were instituted to use this heat to generate high-pressure steam for generating electrical energy, thereby maximizing energy recovery while minimizing process energy use. This combination of a chemical plant and an electrical (or steam) generation system is known

***Table* 4.4** Sulfuric Acid Capacity in the Free World (in thousands of metric tons per day)

	1970	1980	1990 (estimated)
World	250.9	430.9	614.5
United States	92.7	152.7	189.1
Europe	99.1	170.9	200.0
Japan	20.9	27.3	36.4
Canada	10.0	15.5	22.7
Mexico	6.8	8.9	5.6
North Africa	4.0	18.6	35+
Brazil	2.3	7.1	16+

SOURCE: Monsanto Enviro-Chem.

as cogeneration. A modern sulfuric acid plant is, therefore, an electrical generating system. Of course, this secondary function complicates the plant's operating system, but it sharply reduces the cost of the acid produced. Plants have become larger to utilize the economies of large scale; a 2800-t/day plant was brought on stream in 1982.

MANUFACTURE BY THE CONTACT PROCESS. Until 1900, no contact plant had been built in the United States, although this process had become very important in Europe because of the need for oleums and for high-strength acids for sulfonation, particularly in the dye industry. A substantial number of contact plants were built in the period 1900 to 1925, using platinum catalysts. In the middle 1920s, vanadium catalysts came into use and have gradually completely replaced platinum. By 1930, the contact process could compete with the chamber process regardless of the strength of acid desired. Since the mid-1920s most new facilities built have used the contact process with vanadium catalysts.

There have been many improvements both in equipment and catalyst. Typical flowcharts are shown in Figs. 4.3, 4.4, and 4.5. Parts of the process vary considerably, depending upon the type of raw material used. Sulfur-burning plants are the simplest and cheapest since special purification of burner gases to protect the catalyst is not required. In the single-absorption configuration, which was the normal procedure until the 1970s, little attention was directed to planning efficient heat recovery so that all heat evolved by combustion and conversion could be recovered in the form of relatively high-pressure steam. When using other raw materials such as sulfide ores and spent or sludge acids, extensive gas purification is required and the heat evolved in the catalytic reaction is needed to preheat SO_2 gas in heat exchangers prior to catalytic conversion. The heat evolved in roasting the ore or in burning the spent acid usually is recovered in the form of low-pressure steam.

The contact process has been gradually modified to use double absorption (also called double catalyst), which increases yields and reduces stack emission of unconverted SO_2. Recently, U.S. government regulations have specified maximum allowable emissions of SO_2 from acid plants and require that all new plants either use the double-absorption process or else be fitted with stack gas scrubbing systems to achieve comparable emission levels. For sulfur-burning plants, allowable emissions are equivalent to 99.7 percent conversion of SO_2, and for plants using smelter gases to about 99.0 to 99.5 percent conversion. Conversions using the single-absorption contact process were typically about 97 to 98 percent. Although some units use alkali scrubbers on the tail gases to stay within the limit, most new plants use double absorption. In this flow configuration, the gases leaving the first absorbing tower are reheated by heat exchange with the bottom converter gases and reenter the final stage of the converter. Because of the lower content of sulfur trioxide, the reaction

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3$$

is able to proceed farther in the desired direction and the higher recovery of 99.7 percent can be achieved. The gases leaving this final stage are cooled and the SO_3 is absorbed in a final absorber tower.

The heat of combustion of sulfur is utilized in a waste heat boiler or boilers and economizers to generate steam for melting the sulfur and for power purposes around the plant. Steam is one of the products of the plant. Modern plants generate steam at 6 MPa, which can be compared with the 2 MPa of a few years ago. Friedman[17] has made an excellent analysis of the energy use in sulfuric acid plants. The steam generated in the larger sulfur-burning plants

[17]Friedman, Sulfuric Acid Energy Design for the 80's, *Chem. Eng. Prog.* 78 (2) 51 (1982).

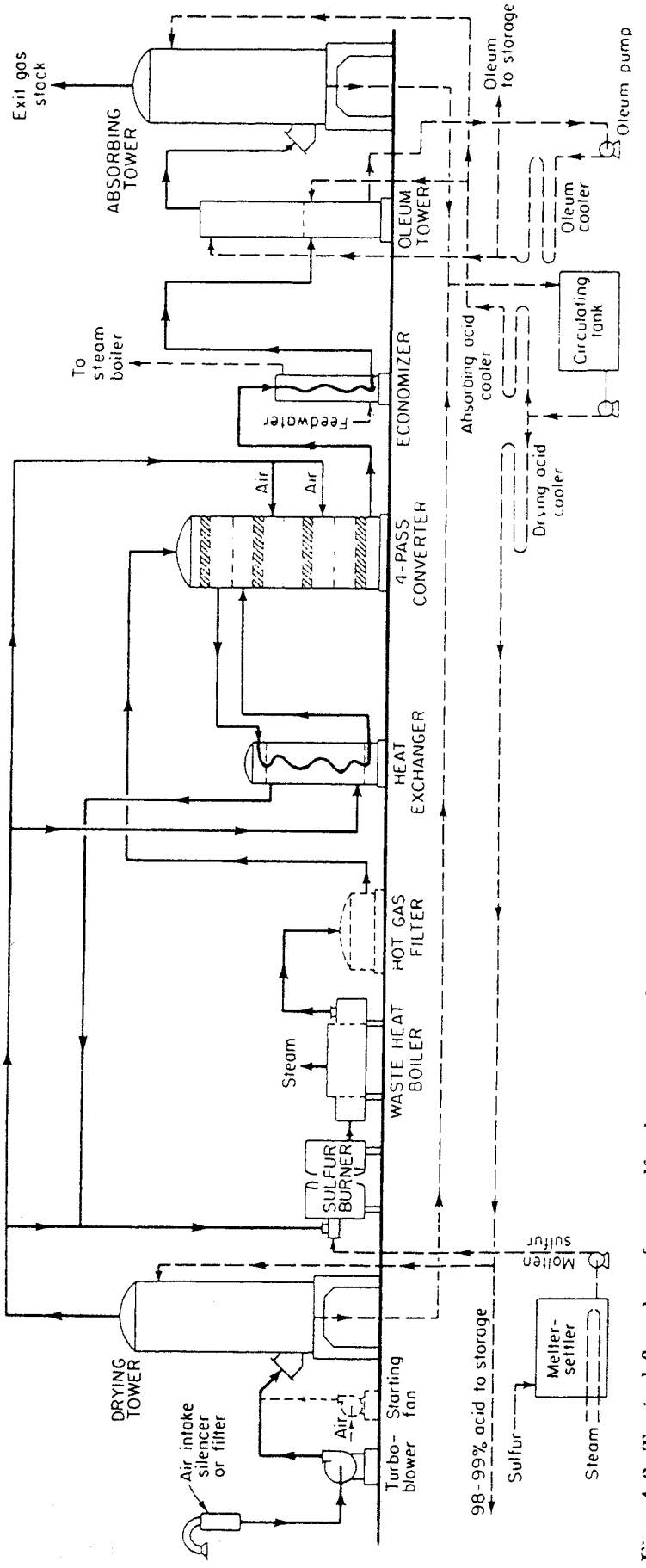


Fig. 4.3. Typical flowchart for a sulfur-burning single-absorption contact sulfuric acid plant with air injection (dilution) cooling between stages. (*Monsanto Enviro-Chem.*)

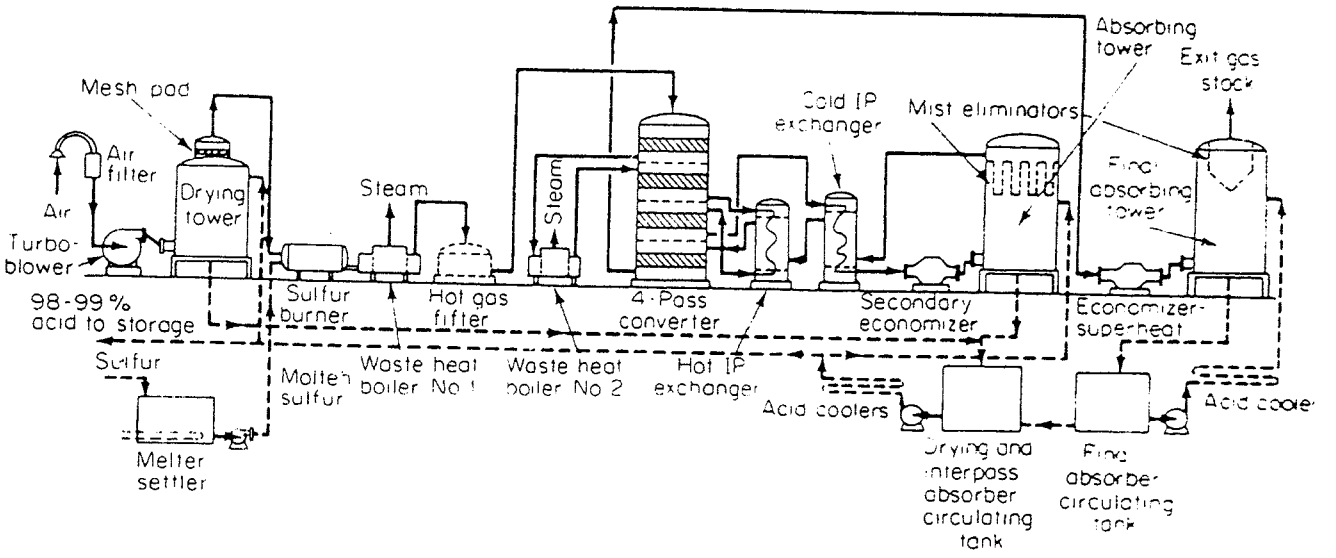


Fig. 4.4. Typical flowchart for a sulfur-burning double-absorption contact sulfuric acid plant. *(Monsanto Enviro-Chem.)*

(Fig. 4.5) normally exceeds 1.3 t per metric ton of acid produced. However, much less steam can be produced when a gas purification system is required. In Sweden[18] a 2200-t day plant delivers 52 MW of heat to a district heating system, saving 35,700 t of fuel oil per day.

The reactions are:

$$S(l) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H = -298.3 \text{ kJ, } 25°C$$

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \qquad \Delta H = -98.3 \text{ kJ, } 25°C$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l) \qquad \Delta H = -130.4 \text{ kJ, } 25°C$$

The oxidation of sulfur dioxide in the converters of the contact plant is an example of the many industrial applications of the principles of physical chemistry.

The reaction from SO_2 to SO_3 is an exothermic reversible reaction. An equilibrium constant[19] for this reaction, calculated from partial pressures according to the law of mass action, may be expressed by:

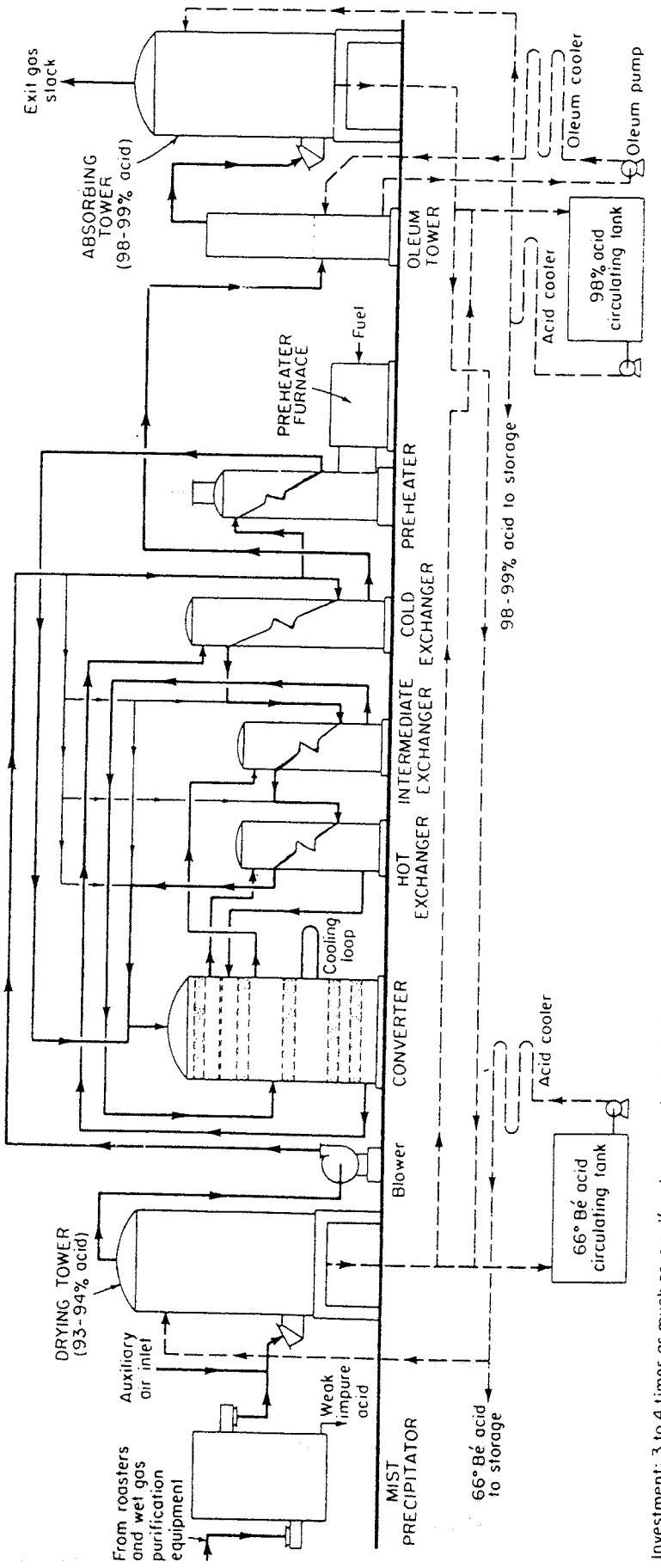
$$K_p = \frac{p_{SO_3}}{p_{SO_2} \times p_{O_2}^{1/2}}$$

Values for K_p have been experimentally determined, based on p in atmospheres, as presented in Table 4.5, and are constant for any given temperature. These experimental values are in satisfactory agreement with the values of K_p calculated from thermodynamic data.

Figure 4.6 shows the equilibrium conversion of SO_2 to SO_3 as a function of temperature for two feeds of different initial SO_2 concentrations. These equilibrium conversions were calculated from the experimental values of K_p (Table 4.5), assuming that all gases are ideal and that the total pressure is 101 kPa (1 atm).

[18]The Changing Sulfuric Acid Industry, *Chem. Week* 130 (6) 40 (1982).

[19]Duecker and West, op. cit. p. 135 ff.



Investment: 3 to 4 times as much as in sulfur-burning plant including roasters and gas purifiers.

Fig. 4.5. Typical flowchart for an ore-roasting single-absorption contact sulfuric acid plant (*Monsanto Enviro-Chem.*)

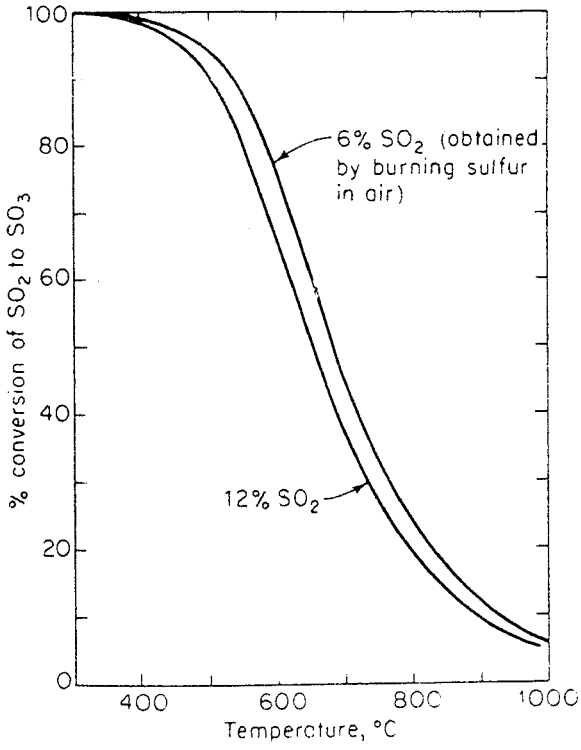


Fig. 4.6. Equilibrium-temperature relation for SO_2 conversion to SO_3. *(Monsanto Enviro-Chem.)*

The equilibrium conversion data in Fig. 19.6 show that the conversion of sulfur dioxide decreases with an increase in temperature. For that reason, it is desirable to carry out the reaction at as low a temperature as practicable. At 400°C, where from Fig. 4.6 the *equilibrium* condition is seen to be very favorable, being almost 100 percent, the *rate* of attainment of this equilibrium is slow. The rate at 500°C is 10 to 100 times faster than at 400°C, at 550°C, it is still faster. Since the reverse reaction, $SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$, does not become appreciable until 550°C, it is advisable to run the reaction initially at this temperature in order to get high rates, giving a maximum conversion with a minimum of catalyst.[20] There is here the usual conflict between favorable conversion equilibrium at lower temperatures and favorable rates at higher temperatures. The actual procedure in a contact plant takes advantage of both rate and equilibrium considerations by first allowing the gases to enter over a part of the catalyst at about 425 to 440°C, and then allowing the temperature to increase adiabatically as the reaction proceeds. The reaction rate increases as the temperature rises, but then begins

[20]Lewis and Ries, Influence of Reaction Rate on Operating Conditions in Contact Sulfuric Acid Manufacture, *Ind. Eng. Chem.* **17**, 593 (1925); **19**, 830 (1927).

***Table* 4.5** Equilibrium Constants for Sulfur Dioxide Oxidation

Temperature, °C	K_p	Temperature, °C	K_p
400	397	800	0.915
500	48.1	900	0.384
600	9.53	1000	0.1845
700	2.63	1100	0.0980

SOURCE: Z. *Elektrochem* 11 373 (1905).

to slow down as equilibrium is approached. The reaction essentially stops when about 60 to 70 percent of the SO_2 has been converted, at a temperature in the vicinity of 600°C. Then the gas, before it passes over the remainder of the catalyst, is cooled in a heat exchanger, in a waste heat boiler, or by other means until the temperature of the gases passing over the last portion of the catalyst is not over 430°C. The yields using this procedure are 97 to 98 percent, and the overall reaction rate is very rapid. Figures 4.3, 4.4, 4.5, and 4.7 illustrate how these conditions are applied in practice and how the heat of reaction is used.

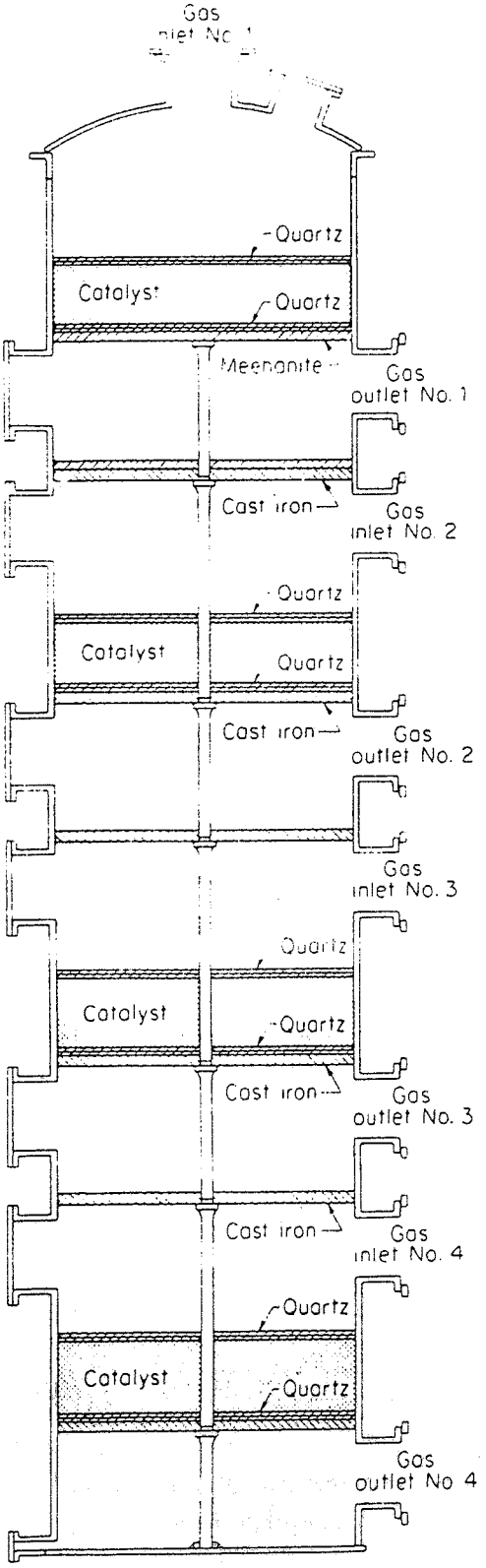


Fig. 4.7. Monsanto four-pass converter. In plants in which cold SO_2 gas must be heated by means of heat in the SO_2 gas, each of the four gas outlets except No. 3 is connected to a tubular heat exchanger. Each of the gas outlets except No. 4 is for the return connection from the exchanger. Cas outlet No. 3 and inlet No. 4 are connected to a small flue cooler from which the heat may be discarded because it is small in amount and not needed for preheating SO_2 gas (Fig. 19.5). In sulfur-burning plants, many variations are used for SO_3 gas cooling. Any of the gas outlets may be connected to a heat exchanger, waste heat boiler, steam superheater, or other cooling equipment. Any one of them may also be used for the injection of cold, dry air (Fig. 19.3). *(Monsanto Enviro-Chem.)*

Rewriting the expression for K_p in terms of mole fractions and total pressures for the equation $2SO_2 + O_2 = 2SO_3$, we get:

$$K_p = \frac{N \times n_{SO_3}^2}{n_{SO_2}^2 \times n_{O_2} \times P}$$

where n = number of moles of each component, N = total moles, and P = total pressure

By rearranging, we get

$$n_{SO_3}^2 = \frac{n_{SO_2}^2 \times n_{O_2} \times K_p \times P}{N}$$

This expression shows that an increase in either SO_2 or oxygen increases the conversion to SO_3. Oxygen enrichment of converter gas was attempted but was not a commercial success. If the concentration of oxygen in the burner gas increases, that of SO_2 decreases, and vice versa. An increase in pressure, according to the principle of Le Chatelier, also increases the conversion to SO_3, but the effect is not large. A superatmospheric plant[21] has recently been built in France, and some advantages have been claimed. However, the expected cost savings appear not to have materialized. The number of moles of SO_3 formed at equilibrium is inversely proportional to N, the total number of moles in the above equation. This shows that if the mixture of gases going through the converter is diluted with an inert gas, such as nitrogen, the conversion to SO_3 is decreased

The conversion of SO_2 to SO_3 is a reversible reaction. If a portion of the SO_3 is removed, more SO_2 will be converted in order to reestablish the equilibrium. This fact is being used to increase the overall conversion efficiency and decrease the quantity of SO_2 being released to the atmosphere (Fig. 4.4). The gases leaving the converter (Fig. 4.7), after having passed through two or three layers of catalyst, are cooled and passed through an intermediate absorber tower where some of the SO_3 is removed. Mist eliminators are essential when interpass cooling is used. The gases leaving this tower are then reheated, and they flow through the remaining layers of catalyst in the converter. The gases are then cooled and passed through the final absorber tower before being permitted to flow into the atmosphere. In this manner more than 99.7 percent of the total SO_2 is converted into SO_3 and subsequently into product sulfuric acid

CATALYSTS.[22] In all catalystic reactions, the function of the catalyst is to increase the *rate* of the reactions. A typical sulfur dioxide-converting catalyst consists of a diatomaceous earth impregnated with upward of 7% V_2O_5. Commercial catalysts contain appreciable amounts of potassium salts (sulfates, pyrosulfates, etc.) in addition to V_2O_5. At operating temperatures the active ingredient is a molten salt held in a porous silica pellet. Sometimes two grades are charged into the converter, a less active but harder type being used in the first pass of the converter and a more active but softer type in passes subsequent to the first. These catalysts are long lived, up to 20 years, and are not subject to poisoning, except for fluorine, which damages the siliceous carrier. Trouble is also encountered with arsenic, and vanadium can be

[21]Bauer and Vidon, The Ugine Kuhlmann Pressure Process, *Chem. Eng. Prog.* 74 (9) 68 (1978).

[22]Fairlie, op. cit., discusses patents and patent litigation. Duecker and West also give some later details. Both are pretty well out of date.

removed as volatile oxychlorides if large amounts of chlorides are present. Plugging with dust and acid mist can be a problem . Dust can be removed from first-pass catalyst by removal and screening. Conversions are high, up to 98 percent, depending on the SO_2 gas strength and on O_2/SO_2 ratios in single-absorption plants and up to 99.8 in double-absorption-type plants. Clean SO_2 must, of course, be provided. Monsanto Enviro-Chem, American Cyanamid, Halder-Topsoe, and other vanadium catalysts are extensively used.

The higher conversions accomplished in double-absorption plants are not the result of increased catalytic efficiency per se, but are accomplished by passing the gas through the converter a second time after the majority of the sulfur trioxide has been scrubbed out of the gas, thus the equilibrium is disturbed.

Iron oxide and platinum catalysts were used before the 1930s but are now normally not used, having been replaced by vanadium. Catalysts are formed into larger cylindrical shapes and into hollow cylinders in order to reduce the pressure drop in the converter while retaining a large superficial surface. There are changes in the formulation, but present-day catalysts are all vanadium-impregnated diatomaceous earth.

Contact Process Equipment

Duecker and West[23] detail the many variations in the equipment employed and include materials of construction. All recent plants have the "outdoor" type of construction, which reduces initial capital investment. These plants are insulated where necessary to conserve heat but are otherwise completely exposed to the elements, often having only the control room enclosed.

BURNERS. Sulfur and some sulfide ores are the usual raw materials. Because of its superior purity and lower transportation costs, sulfur is frequently brought in and stored in molten condition. It is then pumped from a storage tank through heated lines and sprayed into a furnace using burners very similar to those usually used for burning fuel oil. In sulfur burning plants, the strength of the SO_2 gas allowed to enter the converter has increased over the years from a strength of about 8% SO_2 by volume to the present practice of 11% SO_2 with the newest plants handling 12% successfully.

Ores are burned in fluidized beds or rotary roasters.

TREATMENT OF THE BURNER GAS. Sulfur dioxide burner gas may contain carbon dioxide, nitrogen, such impurities as chlorine, arsenic, fluorine, and a small amount of dust. Arsenic and fluorine are present only when materials other than elemental sulfur are burned. To prevent corrosion from the burner gas, it is customary to dry the air for burning the sulfur, and oxidizing the SO_2 until the moisture content is below 35 mg/m^3, as shown in Figs. 4.3 and 4.4, and to dry the roaster gases before oxidizing the SO_2 as is shown in Fig. 4.5. Such drying is done in towers, usually with 93 to 98% sulfuric acid. The sulfur burner gas has much of its heat removed in waste heat boilers for the generation of steam. If sulfide ore is roasted, efficient dust collectors, cooling and scrubbing towers, and electrostatic mist precipitators may be added.

HEAT EXCHANGERS AND COOLERS. Before the gases are fed to the first stage of the converter, they are adjusted to the minimum temperature at which the catalyst rapidly increases

[23]Duecker and West, op. cit., discuss burners in chaps. 8 and 9, converters in chap. 14.

the speed of the reaction, usually 425 to 440°C. The gases must be cooled between catalyst stages to achieve high conversion. For this purpose, cold air may be introduced (to cool by dilution), or boilers, steam superheaters, or tubular heat exchangers may be employed. Heat exchangers usually consist of large cylinders containing many small tubes. The SO_3-containing gases usually pass through the tubes and the SO_2-containing gases surround the tubes.

CONVERTERS. The chemical conversion of sulfur dioxide to sulfur trioxide is designed to maximize the conversion by taking into consideration that:

1. Equilibrium is an inverse function of temperature and a direct function of the oxygen to sulfur dioxide ratio.
2. Rate of reaction is a direct function of temperature.
3. Gas composition and amount of catalyst affect the rate of conversion and the kinetics of the reaction.
4. Removal of sulfur trioxide formed allows more sulfur dioxide to be converted.

The commercialization of these basic conditions makes possible high overall conversion by using a multipass converter wherein, at an entering temperature of 425 to 440°C (the ignition temperature), the major part of the conversion (60 to 75 percent) is obtained in the first catalyst bed with an exit temperature of 600°C or more, depending largely on the concentration of SO_2 in the gas. Table 4.6 gives the temperatures and percent conversions for each stage of a four-pass converter.[24] The successive lowering of the temperature between stages ensures an overall higher conversion. Conversion in a four-stage converter of a single-absorption plant is 98 percent or slightly higher. In the multipass converter shown, about 20 percent of the total catalyst is in the first stage, where 70 to 75 percent of the conversion may take place.

[24]Slin'ko and Beskov, Calculation of Contact Equipment with Adiabatic Catalyst Layers for Oxidation of Sulfur Dioxide, *Int. Chem. Eng.* 2 (3) 388 (1962).

Table 4.6 Temperatures and Conversions in Each Stage of a Monsanto Converter (using relatively rich SO_2 gas from sulfur)

Location	Temperature, °C	Equivalent Conversion, %
Gas entering first pass	410.0	
Gas leaving first pass	601.8	
Rise in temperature	191.8	74.0
Gas entering second pass	438.0	
Gas leaving second pass	485.3	
Rise in temperature	47.3	18.4
Gas entering third pass	432	
Gas leaving third pass	443	
Rise in temperature	11	4.3
Gas entering fourth pass	427.0	
Gas leaving fourth pass	430.3	
Rise in temperature	3.3	1.3
Total rise	253.4	98.0

SOURCE: Based on Duecker and West, *Manufacture of Sulfuric Acid*, ACS Monograph 144, Reinhold, New York, 1959, p. 252.

In the converter shown in Fig 4.7, the hot conversion gases are progressively cooled between stages and, in a double-absorption plant, after leaving the third stage, pass through heat exchangers and sometimes an economizer, before the SO_3-containing gas enters the first 98 to 99% absorbing tower, having previously passed through an oleum tower if this product is desired. The gas leaving the 98 to 99% tower is reheated in heat exchangers and reenters the converter at the fourth pass. On leaving this, it again goes through heat exchangers and or an economizer to enter the final 98 to 99% absorbing tower. The converter depicted in Fig. 4.7 is provided with trays for supporting the catalyst and manholes for access to it. Converters have usually been made of cast iron and aluminum-coated steel, but stainless steel is now the preferred material of construction. Pressure drop through the converter must be minimized to reduce power consumption. The converter is the "heart" of a contact sulfuric acid plant and there are many variables. All these must be optimized to secure the maximum yield and profit. Converters as large as 14 m in diameter are being built. Studies have been made regarding use of computers[25] for converter design.

SULFUR TRIOXIDE ABSORBERS. It has been known for a long time that a concentration of acid between 98.5 and 99% sulfuric acid is the most efficient agent for the absorption of sulfur trioxide, probably because acid of this strength has a lower vapor pressure than any other concentration. Acid of this strength is used in the intermediate and final absorbers for essentially complete absorption of the SO_3 before the partially converted gas reenters the converter and the waste gas is vented to the atmosphere. Water cannot be used because direct contact of sulfur trioxide and water results in an acid mist that is almost impossible to absorb. Since the absorbing acid is continuously becoming more concentrated, it is necessary to provide some means of diluting that part of the acid which is discharged from the absorbers and which is to be recirculated. The recirculated acid is diluted by adding dilute sulfuric acid or water in the amount required, cooling the absorbing acid, and withdrawing any excess acid from the system for sale.

The 20% oleum is made in an oleum absorber[26] as shown in Figs. 4.3 and 4.5, if the plant includes such an oleum tower, by adding 98 to 99% acid to the oleum which is circulating over this tower. If an oleum of 60 to 65% is wanted, it may be prepared by producing 30 to 35% oleum in the tower and distilling it in steel boilers. The trioxide driven off may be absorbed in a separate stream of oleum or condensed and blended with other oleum to get the desired concentration. The usual oleum tower may be able to produce 30 to 40% oleum in smaller quantities. If full capacity for such oleum is required, it may be necessary to use two oleum towers in series ahead of the first 98 to 99% absorber. Most absorbers are equipped with mist eliminators, such as Monsanto's Enviro-Chem.

The tower, which dries the air or SO_2 gas by contacting it with circulating 98 to 99% acid, is made of steel lined with acid-proof brick and packed with ceramic shapes to effect intimate contact of acid with air or gas. The air or gas enters the lower part of the tower and leaves by a flue at the top. A 98.5 to 99% absorbing tower 7.1 m in diameter, inside the lining, with a packed volume of 200 m^3 and an acid flow of approximately 9.5 m^3/min can readily absorb 909 t of sulfur trioxide per 24 h with an apparent gas velocity of 62 cm/s measured at standard conditions of 0°C and 101 kPa. For oleum, the steel tower need not be lined.

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[25]Homme and Othmer, Sulfuric Acid, Optimized Conditions in Contact Manufacture, *Ind. Eng. Chem.* **53** 979 (1961); Shannon Digital Computer, *Chem. Eng.* **72** (20) 84 (1965); Shannon, Computer Simulation, *Chem. Eng. Prog.* **62** (4) 49 (1966); Donovan, Palermo, and Smith, Sulfuric Acid Converter Optimization, *Chem. Eng. Prog.* **74** (9) 51 (1978).

[26]Duecker and West, op. cit., pp. 226, 255

BLOWERS. Blowers are used to propel the air and/or sulfur-containing gases (SO_2 and SO_3) through the processing equipment. These are located in the flow so that they can handle either air or sulfur dioxide–containing gas (usually after the air or gas has passed through the drying tower). They are electric motor– or steam turbine–driven single-stage centrifugal compressors of cast iron, cast steel, or fabricated steel. Pressure differentials as high as 55 kPa are obtained using only one main blower in each contact acid plant, with capacities up to 3000 t/day. The blower is the major energy consumer in the plant.

ACID PUMPS. Vertical shaft centrifugal submerged pumps of cast iron construction with alloy impellers and shafts are used to circulate acid over the drying and absorption towers. The pumps are usually immersed in brick-lined steel pump tanks within the process area. These may be driven by electric motors or steam turbines.

For transferring acid from one place to another, horizontal shaft pumps of alloy construction are generally used.

SULFUR PUMPS. Vertical shaft submerged centrifugal pumps of cast iron construction are also used to pump sulfur from a pit to the atomizers in the sulfur burner. These pumps have steam-jacketed discharge piping to prevent cooling and solidification of the sulfur, which has a melting point of about 115°C.

ACID COOLERS. The acid circulating over the absorbing towers must be cooled to remove the heat of absorption and the sensible heat of the incoming gas. The acid circulating over the drying tower must be cooled to remove the heat of dilution and heat of condensation of moisture from the incoming gas or air. Formerly this was done by passing water over coils or special cooler sections of cast iron through which the circulating acid was pumped. Recently, shell-and-tube–type heat exchangers of alloy steel, often anodically protected, have been introduced to replace cast iron. Plate coolers of special alloys are also being used. Cast iron (having numerous flanged joints and potential places for acid leakage) has been replaced by these newer coolers in most plants now being built.

GAS PURIFICATION. Plants which must handle impure sulfur dioxide gases, such as those leaving smelters, ore roasters, and other processes, may include waste heat boilers (for heat recovery while cooling the gases), electrostatic dust precipitators (for recovering valuable calcine while also cleaning the gases), scrubbing or wash towers (for further cooling the gases in order to adjust the temperature for water balance in the acid plant while also removing additional dust), and finally electrostatic mist precipitators for removal of acid mist and residual dust and fume. The gases are then ready to enter the drying tower.

MATERIALS OF CONSTRUCTION. After the moisture has been removed in the drying tower, ordinary steel and cast iron are satisfactory materials of construction for use in handling the gas or air and the strong acid. Because of the corrosive and erosive effect of hot acid on steel, the drying and absorbing towers and the acid pump tanks associated with these towers are constructed of brick-lined steel. The brick lining of the oleum tower and pump tank may be omitted if desired. Good quality cast iron is the material normally used as piping for the acid circulating over the drying and 98 to 99% absorbing towers. Cast iron is not suitable for use in the oleum system. For reasons not yet understood, cast iron fails catastrophically in oleum service.

In the gas purification system, steel is used for handling sulfur dioxide gases having temperatures above the acid dew point. For temperatures below the acid dew point and for

liquids, lead, lead-lined steel, with or without a brick lining, alloy steels, and plastic materials are used for specific service conditions. In the United States, the mist precipitators are usually fabricated of lead, with lead collector tubes. Tubular mist precipitators of plastic materials have been built in Europe.

The weak acid coolers in the gas purification system cannot be fabricated of cast iron or steel, which would corrode rapidly. Instead of the lead coil-type coolers used in older plants, modern plants may use shell and tube heat exchangers of graphite or plate-type coolers of special alloys.

PLANT COST. It is difficult to give the approximate general cost of a plant, because of variations in design and in prices in different places and because of continuing inflation. Yet it may be said that a modern double-absorption sulfur-burning contact plant producing 1800 t/day, 100% H_2SO_4 basis, cost roughly $25 million in the early 1980s. To this figure must be added whatever is required for storage, extension of utilities, and necessary off site facilities. A metallurgical-type plant burning sulfide ores, such as that shown in Fig. 4.5, would cost three or four times the figure given for a sulfur-burning plant, since it would include ore roaster and extensive gas cooling and purification facilities.

Figure 4.8 is a photograph of the 2800-t/day sulfur-burning sulfuric acid plant at the Texasgulf Inc. phosphate operation in North Carolina, which started operating early in 1982.

SULFUR TRIOXIDE[27]

Liquid sulfur trioxide is used for sulfonation, especially in the manufacture of detergents (Chap. 29). In the past, the difficulty was the instability of the sulfur trioxide. However, under the trade name Sulfans, stabilized forms of sulfur trioxide are commercially available; crystallization or conversion to a polymer is inhibited by several patented inhibitors, such as boron compounds, methane sulfonyl chloride, sulfur, tellurium, and phosphorus oxychloride.[28] This product is manufactured by distillation of strong oleums.

RECOVERY OF USED SULFURIC ACID

Much used sulfuric acid is recovered for recycling. This used acid is often referred to as waste acid, a misnomer. Many users do not consume the acid but dilute and contaminate it. Some of it can be recovered and reused at a cheaper cost than virgin (new) acid. Some of it must be recovered in order to meet environmental restrictions or to avoid the cost of neutralization. About 2×10^6 t of spent acid is reused each year: (1) spent alkylation acid catalyst is black, but still relatively strong, and not too heavily contaminated (about 90% H_2SO_4, 5% water, and 5% hydrocarbons), (2) nitration spent acid is diluted and only slightly contaminated, (3) spent sludge acids result from petroleum refining. These latter are usually dirty, low in acidity,

[27]Enter, Trioxide Intermediates, *Chem. Week* **102** (8) 31 (1965).

[28]*McGraw-Hill Encyclopedia of Science and Technology*, vol. 13, McGraw Hill, New York, 1982, p. 299.

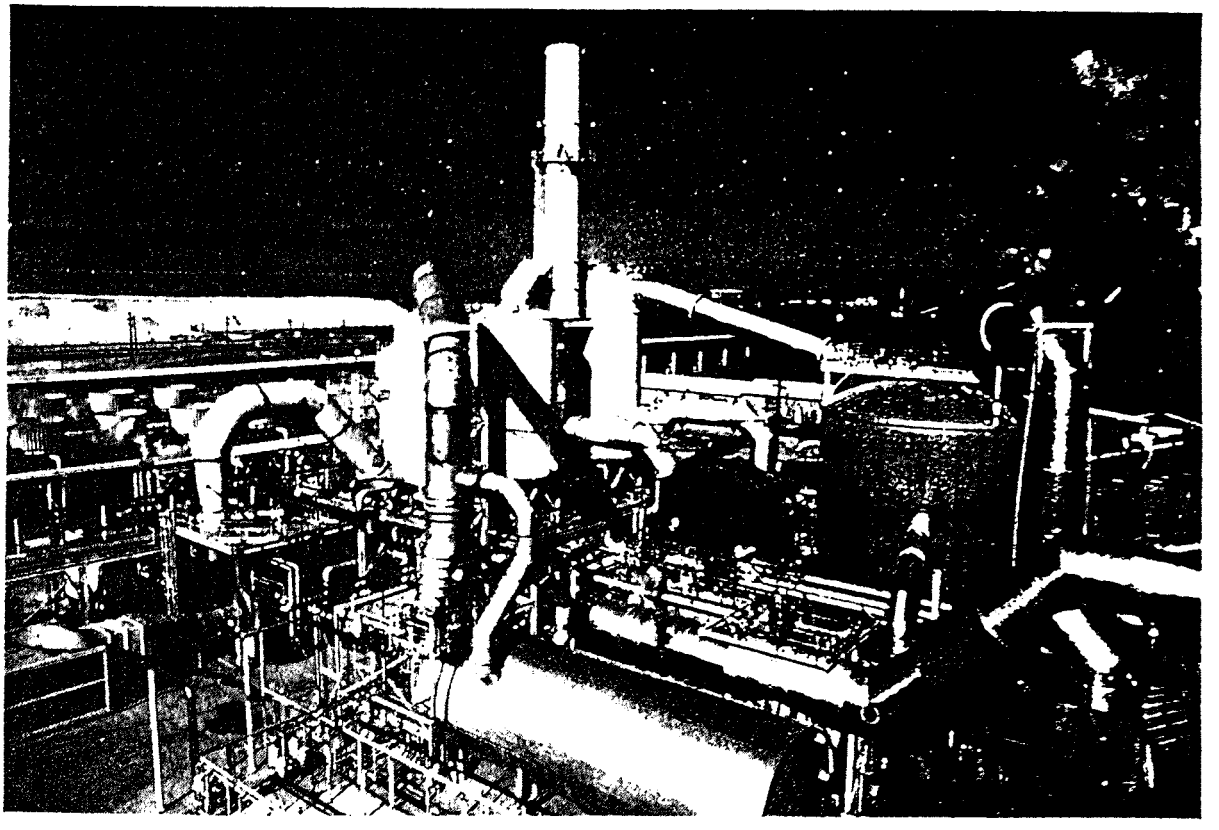

Fig. 4.8. Double-absorption, energy-efficient sulfuric acid plant with a capacity of 2800 t/day. (*Texasgulf, Inc.*)

heavily contaminated, and many contain up to 75% H_2SO_4 and up to 20% or more hydrocarbons, the balance being water. Occasionally, they can be added in small percentages to spent alkylation acid or reduced to sulfur dioxide by heat with coke as a by-product, but the process is expensive. Other spent acids, which have been used for their ability to absorb water, such as in the production of alcohols, in drying hydrochloric acid gas, etc., can sometimes be recovered by simple concentration.

Some sulfuric acid is still being used in the steel industry for pickling, that is, the preparation of plate for tinning or galvanizing. Because of the need to eliminate the discharge of spent liquors into streams, and because of the difficulty in treating such liquors for the recovery of the acid values, sulfuric acid is being replaced by hydrochloric acid. Spent hydrochloric liquor can be treated to recover acid values and to avoid stream pollution.

A residual liquor similar to steel mill pickle liquor is obtained from titanium pigment plants which use sulfuric acid to produce titanium dioxide from ilmenite. Most titanium dioxide pigment is made by the chloride route to avoid the disposal problem associated with the use of sulfuric acid.

Spent alkylation acid is being economically recovered[29] by atomizing it, burning it in a furnace, and cooling and purifying the gases in a manner similar to that used for smelter gases. The sulfur dioxide gas resulting from the combustion is then converted into new, virgin-pure acid in a contact plant.

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[29]Galstaun, Steigerwald, Ludwig, and Garrison, What Does it Cost to Desulfurize Fuel Oil? *Chem. Eng. Prog.* **61** (9) 49 (1965); Mills and Perry, Fossil Fuel Yields Power plus Pollution, *CHEMTECH* **13** (3) 53 (1973); Robinson and Robbins, Gaseous Sulfur Pollutants from Urban and Natural Sources, *J. Air Pollut. Control Assoc.* **20** (4) 233 (1970).

Nitration spent acid is usually recovered by concentration.

Petroleum sludge acids may be blended with spent alkylation acid, thus supplying any fuel deficiency in the alkylation acid. Before processes were available for recovering alkylation spent acid (and before it was produced in large quantity), some petroleum sludges were recovered by diluting (hydrolyzing) them with water and increasing the temperature either at ambient or superatmospheric pressure. The hydrocarbon upper layer would then be decanted and the lower layer concentrated for acid recovery.

SULFUR POLLUTION

The reduction of pollution by sulfur and sulfur compounds has been extensively studied with the hope of eventual recovery for reuse.[30] Fuel desulfurization usually yields sulfur as hydrogen sulfide. Sulfur dioxide from nonferrous metal smelting or fuel combustion is most economically recovered as sulfuric acid, and less often as liquid sulfur dioxide, sulfur, or sulfate salts. Sulfuric acid has long been made from the richer gases at smelters with access to markets.

Large tonnages of sulfur are recovered from gaseous and light liquid petroleum fractions. In the United States, 23.4×10^6 t of sulfur dioxide is emitted from fuel combustion, compared with 2.3×10^6 recovered; 7.0×10^6 t is emitted from industrial processes, mainly smelting, compared with 0.8×10^6 recovered. Most of the sources are too small, too dilute, or too isolated for economical recovery. Nevertheless, new air pollution regulations are forcing smelters to recover up to 90 percent of input sulfur and are sharply limiting emissions of sulfur dioxide from fuel combustion. These regulations have brought about new facilities for desulfurizing fuel oils, a revived interest in low-sulfur liquid and gaseous fuels from coal, and many demonstration plants for removing sulfur dioxide from power plant waste gases.[31]

Emissions from new sulfuric acid plants are limited to 2 kg of sulfur dioxide and 75 g of acid mist per metric ton of acid made.

Recovery by the Claus process is never 100 percent because the reaction is an equilibrium one. Regulations controlling allowable emissions of sulfur dioxide from these plants vary from place to place and are often stricter than for larger plants. Many new plants are built with one more converter than is shown in Fig. 4 .2, and various tail gas cleanup units are being installed in both new and old plants.

Continuous copper smelters, such as the Outokumpu Oy, Mitsubishi, and Noranda processes, are being installed in order to recover high-strength sulfur dioxide gases suitable for efficient conversion into sulfuric acid, thus reducing atmospheric pollution.

Emissions from new installations of large coal-fired steam boilers are now limited to 516 g SO_2 per 1000 MJ of fuel burned. Usually the excess SO_2 is removed in tail gas scrubbers, and the resulting sulfates and/or sulfites are rejected without recovery of the sulfur values.

Pollution of streams and other sources of potable water is controlled by regulations limiting

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[30]Schuit and Gates, Chemistry and Engineering of Catalytic Hydrodesulfurization, *AIChE J.* **19** (3) 417 (1973); Semrau, Control of Sulfur Oxide Emissions form Primary Copper, Lead, and Zinc Smelters, *J. Air Pollut. Control Assoc.* **21** 185 (1971); Conn, Low BTU Gas for Power Plants, *Chem. Eng. Prog.* 69 (12) 56 (1973).

[31]Davis, Sulfur Dioxide Absorbed from Tail Gas with Sodium Sulfite, *Chem. Eng.* **78** (27) 43 (1971); Hyne, Methods for Desulfurization of Effluent Gas Streams, *Oil Gas J.* **70** (35) 64 (1972); Barry, Reduce Claus Sulfur Emissions, *Hydrocarbon Process.* **51** (4) 102 (1972); Chalmers. Citrate Process Ideal for Claus Tailgas Cleanup, *Hydrocarbon Process.* 53 (4) 75 (1974).

acidity, turbidity, oxygen demand, etc. Discharge of any liquid, gaseous, or solid waste is regulated by federal and local laws which require careful observance. For each particular application, permits to discharge must be obtained, often with great difficulty and at considerable expense.

CONCENTRATION

The literature describes various types of concentrators for sulfuric acid. Weak acid can be concentrated to a somewhat higher strength by immersing a steam-heated lead coil in a lead- or lead-and-brick–lined tank. Strong (98%) acid can be obtained by underfiring cast iron pots. The pots are not corroded provided that the acid is kept strong enough. Most concentration of acid today is accomplished in hot air blown concentrators or in vacuum concentrators using steam or other heat transfer fluids.

An air-blown concentrator[32] is shown in Fig. 4 .9. The burner supplies hot gases at about

[32]Duecker and West, op. cit., p. 340; Smith and Mantius, The Concentration of Sulfuric Acid, *Chem. Eng. Prog.* 78 (2) 78 (1978); Rodger, Developments in the Concentration of Sulfuric Acid, *Chem. Eng. Prog.* 78 (2) 39 (1982).

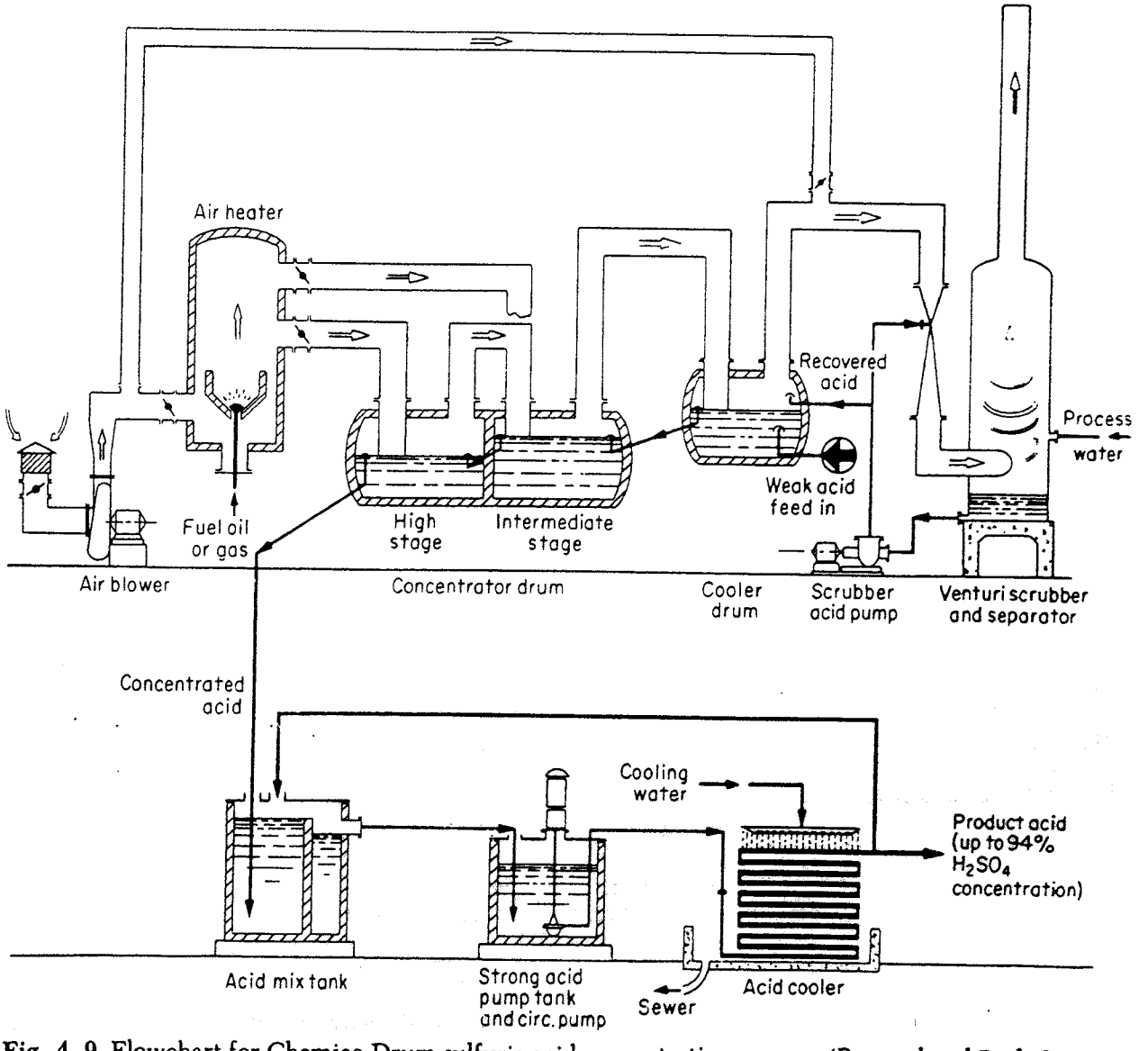

Fig. 4 .9. Flowchart for Chemico Drum sulfuric acid concentration process. *(Barnard and Burk Group.)*

680°C by the combustion of oil or fuel gas. These hot combustion gases are blown countercurrent to the sulfuric acid in two compartments in the concentrating drum and remove water as they bubble through the acid. The off gases at 230 to 250°C from the first compartment of the drum pass to the second compartment, along with a portion of the hot gases from the combustion furnace. They leave at 170 to 180°C to enter a gas-cooling drum, where they are cooled to 100 to 125°C in raising the dilute acid to its boiling point. Since some sulfuric acid is entrained as a mist, the hot gases are passed through a venturi scrubber and a cyclone separator and are washed with feed acid or water for removal of the acid mist before discharge to the atmosphere. This reduces the acid mist to perhaps 35 mg/m^3 and involves considerably less capital investment than an electrostatic mist precipitator. This procedure gives an acid with a final concentration of 93% or just slightly higher. The hot gases, aided by the oxidizing action of the hot sulfuric acid, also burn out many impurities that may be found in spent acid being concentrated. Such air-blown concentrators are, therefore, extensively employed in the concentration of spent nitrating acid from munition works. If spent acid from petroleum purification is being handled, the flow of acid from the rear to the front compartment passes through an intermediate storage tank, where a skimmer removes some of the nonvolatile carbonaceous impurities. The concentrating compartments of the steel drum are lined with lead and acid-proof masonry. In this type of concentrator, the boiling

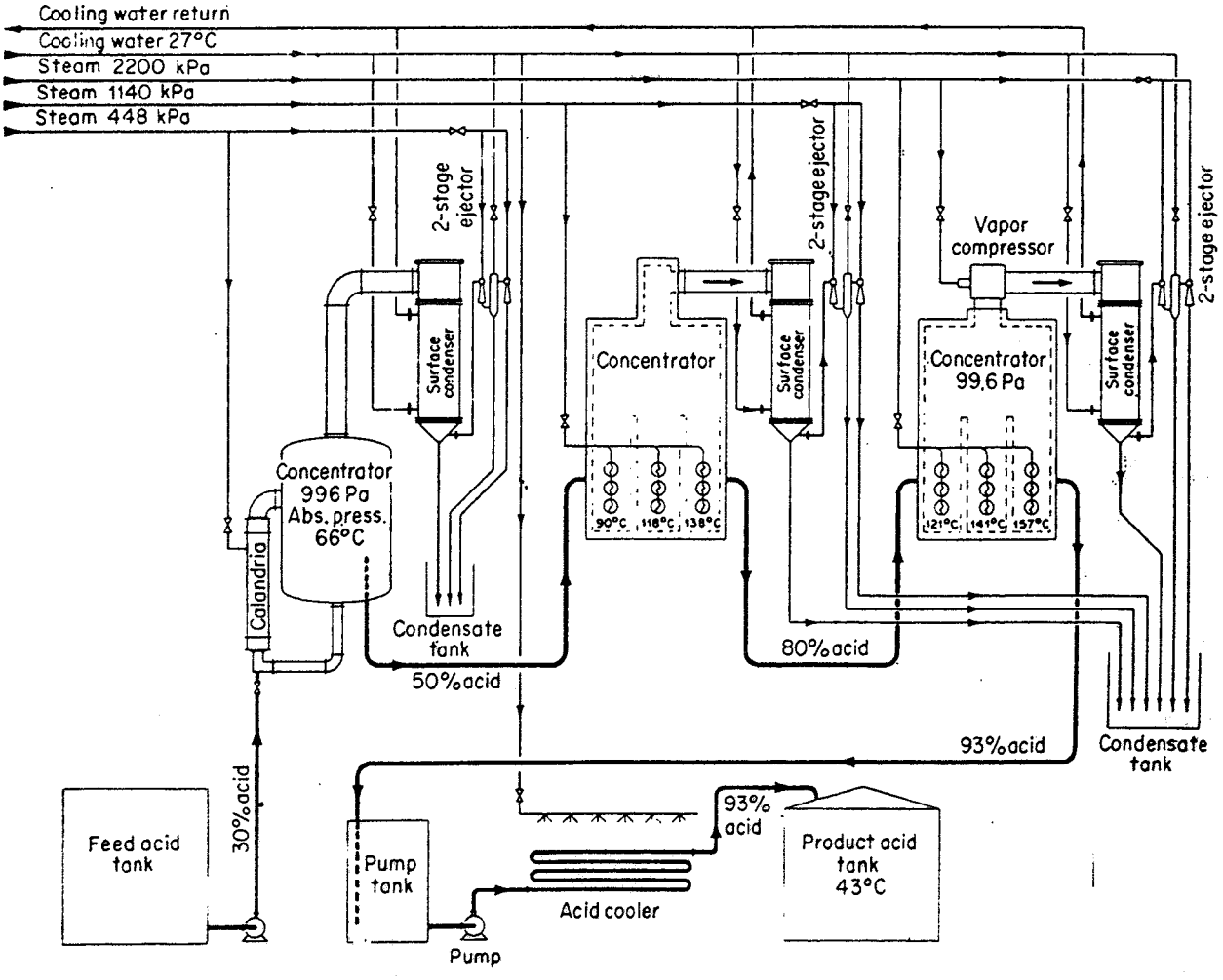

Fig. 4.10. Flowchart for Simonson-Mantius (SM) vacuum sulfuric acid concentration process. *(Barnard and Burk Group.)*

point of the acid is reduced as much as 60°C for 93% acid by the effect of hot air in reducing the partial pressure of the water vapor above the acid.

Simonson-Mantius[33] vacuum concentrators operate at pressures as low as 675 Pa and have long been used to concentrate sulfuric acid up to a maximum strength of 93%. Several types fit different conditions and various concentrations. The SM (formerly Simonson-Mantius) vacuum concentration process uses steam in tantalum indirect heaters to vaporize water from the acid that is maintained under vacuum. The use of vacuum lowers the boiling point of the acid. Any noxious vapors that are carried out of the concentrators are removed in the condensers. No acid fumes or mist escape to the atmosphere. Figure 4 .10 shows a simplified flowchart for a standard SM unit.

Both the Chemico drum concentrator and the SM concentrator are now offered by Barnard and Burk of Mountainside, N.J.

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[33]Burke and Mantius, Concentration of Sulfuric Acid Under Vacuum, *Chem. Eng. Prog.* 43 237 (1947); see also Duecker and West, op. cit., pp. 329 and 335.

Chapter 5

Hydrochloric Acid and Miscellaneous Inorganic Chemicals

HYDROCHLORIC OR MURIATIC ACID

Hydrochloric acid, although not manufactured in such large quantities as sulfuric acid, is an important heavy chemical. Manufacturing techniques have changed, and some is made by the burning of chlorine in hydrogen.

Hydrogen chloride (HCl) is a gas at ordinary temperature and pressure. Aqueous solutions of it are known as *hydrochloric acid* or, if the HCl in solution is of the commercial grade, as *muriatic acid*. The common acids of commerce are 18°Bé (1.142 sp gr) or 27.9% HCl, 20°Bé (1.160 sp gr) or 31.5% HCl, and 22°Bé (1.179 sp gr) or 35.2% HCl,[1] which sell for $35, $55, and $63 per ton, respectively, on the east coast. Anhydrous HCl is available in steel cylinders at a very considerable increase in cost because of the cylinder expense involved.

HISTORICAL. Hydrogen chloride was discovered in the fifteenth century by Basilius Valentinius. Commercial production of hydrochloric acid began in England when legislation was passed prohibiting the indiscriminate discharge of hydrogen chloride into the atmosphere. This legislation forced manufacturers using the Leblanc process for soda ash to absorb the waste hydrogen chloride in water. As more uses for hydrochloric acid were discovered, plants were built solely for its production.

USES AND ECONOMICS. The largest users of hydrochloric acid are the metal, chemical, food, and petroleum industries. Industry experts estimate that the metal industries consume about 47 percent of the acid sold. A breakdown of the remaining uses is: chemical and pharmaceutical manufacturing and processing, 33 percent; food processing, 7 percent; oil well acidizing, 6 percent; and miscellaneous uses, 7 percent.

The major use of hydrochloric acid is in steel pickling (surface treatment to remove mill scale). Prior to 1963 almost all steel was pickled with sulfuric acid. Hydrochloric acid has taken over this market because it reacts faster than sulfuric with mill scale, less base metal is attacked by it, the pickled steel has a better surface for subsequent coating or plating operations, and much smaller quantities of waste pickle liquor are produced.

MANUFACTURE. Hydrochloric acid is obtained from four major sources: as a by-product in the chlorination of both aromatic and aliphatic hydrocarbons, from reacting salt and sulfuric

[1] *Chem. Mark. Rep.* May 17, 1982.

acid, from the combustion of hydrogen and chlorine, and from Hargreaves-type operations ($4NaCl + 2SO_2 + O_2 + 2H_2O \rightarrow 2Na_2SO_4 + 4HCl$). As can be seen from Table 5.1, by-product operations furnish nearly 90 percent of the acid. The old salt–sulfuric acid method and the newer combustion method supply most of the remainder. The Hargreaves process is used by only one company.

Reactions and Energy Requirements. The basic steps in the production of by-product acid include the removal of any unchlorinated hydrocarbon, followed by the absorption of the hydrogen chloride in water. A typical chlorination, for illustration, is:

$$\underset{\text{Benzene}}{C_6H_6} + Cl_2 \longrightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl$$

Since the chlorination of aliphatic and aromatic hydrocarbons evolves large amounts of heat, special equipment is necessary for control of the temperature of reaction.

The synthetic process[2] generates hydrogen chloride by burning chlorine in hydrogen. The purity of the ensuing acid is dependent upon the purity of the hydrogen and chlorine. As both of these gases are available in a very pure state as by-products of the electrolytic process for caustic soda, this synthetic method produces the purest hydrogen chloride of all of the processes.

The reaction between hydrogen and chlorine is highly exothermic and spontaneously goes to completion as soon as it is initiated. The equilibrium mixture contains about 4% by volume free chlorine. As the gases are cooled the free chlorine and free hydrogen combine rapidly so that when 200°C is reached the gas is almost pure HCl. By carefully controlling the operating conditions, a manufacturer can obtain a gas containing 99% HCl. The HCl gas is further purified by absorbing it in water in a tantalum or impervious or impregnated graphite absorber. The aqueous solution is stripped of hydrogen chloride under slight pressure, giving strong gaseous hydrogen chloride which is dehydrated to 99.5% hydrogen chloride by cooling it to −12°C. Large amounts of anhydrous hydrogen chloride are needed for preparing methyl chloride, ethyl chloride, vinyl chloride, and other such compounds.

Hydrochloric acid is extremely corrosive to most metals, and great care must be taken to choose the proper materials for plant construction. Water absorption of the hydrogen chloride made by any of the processes liberates about 1625 kJ/kg of hydrogen chloride absorbed. This heat[3] must be taken away in the absorber, or the efficiency will be low. Figure 5.2 illustrates the design of an absorber made from graphite.

[2]ECT, 3d ed., vol. 12, 1980, p. 983.

[3]Naidel, Hydrogen Chloride Production in Graphite Vessels, *Chem. Eng. Prog.* 69 (2) 53 (1973); Hulswitt, Adiabatic and Falling Film Absorption of Hydrogen Chloride, *Chem. Eng. Prog.* 69 (2) 50 (1973).

Table 5.1 U.S. Production of Hydrochloric Acid (in thousands of metric tons)

Source	1950	1960	1970	1978	1981
Salt and sulfuric acid	148	82	113	86	80
Chlorine and hydrogen	100	133	85	161	212
By-product and other	308	658	1614	2245	2042
Total	556	873	1812	2492	2334

SOURCE: U.S. Bureau of the Census.

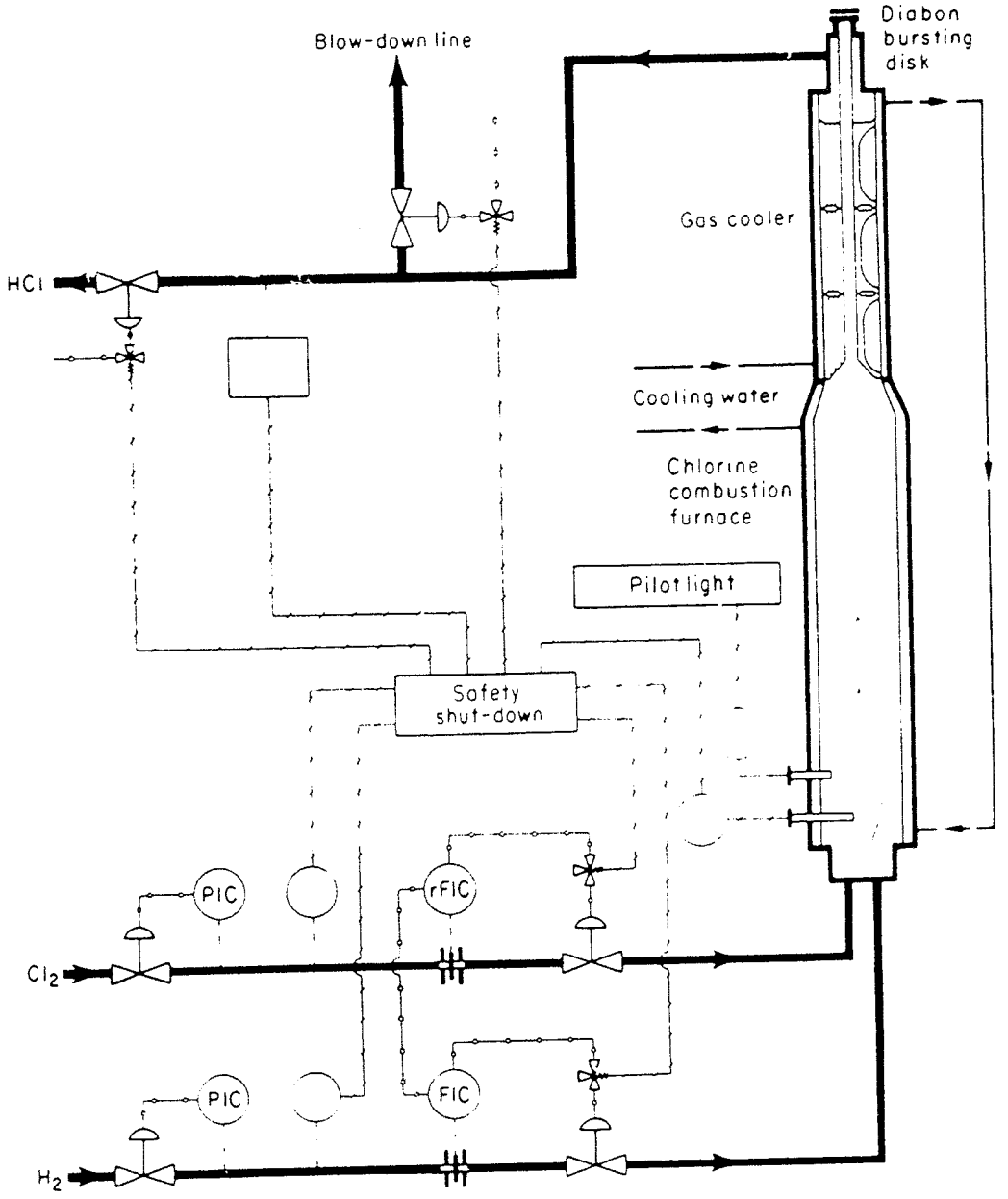

Fig. 5.1. Chlorine combustion furnace. *(SIGRI Elektrographit GMBH.)*

BROMINE

Bromine is a member of the halogen family and is a heavy, dark-red liquid. It is much less common and more expensive than chlorine.

HISTORICAL. In 1824, 15 years after the discovery of iodine, bromine was discovered by Balard, a French chemist, who obtained it from mother liquor left after separating salt from seawater by evaporation. Its manufacture from the Stassfurt deposits of carnallite was begun in 1865, from the $MgBr_2$ in the liquors left after working up $MgCl_2$ and KCl. Today Ethyl Dow operates the largest plant at Freeport, Tex. (Fig. 5.3.), built during World War II.

USES AND ECONOMICS. About 60 percent of the domestic bromine output is used in the manufacture of ethylene dibromide for antiknock fluids.[4] This bromine compound prevents

[4] *Chem. Week* 127 (6) 53 (1980); 128 (12) 26 (1981); *Chem. Mark. Rep.* April 26, 1982; *Chem. Bus.* p. 24, May 3, 1982.

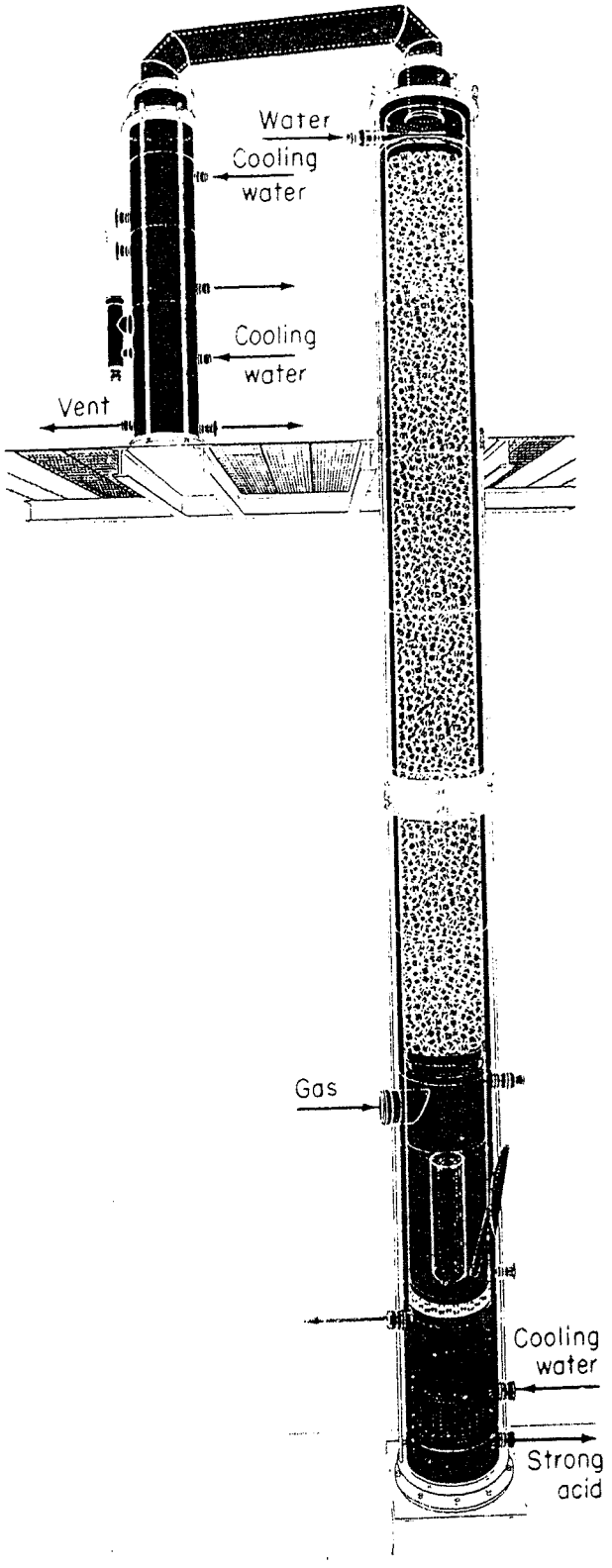

Fig. 5 .2. Diagram of an all-carbon (Diabon) hydrochloric acid, adiabatic absorption tower and cooler. *(SIGRI Elektrographit GMBH.)*

lead oxide deposits in engines which would otherwise result from tetraethyllead (TEL). The appearance of compact cars and jet-fuel airplanes has interrupted TEL and ethylene dibromide production. The Clean Air Act of 1970 mandated air quality standards that caused the EPA to make a commitment to eliminate 60 to 65 percent of lead antiknock compounds from gasoline by 1979. This further reduced the amount of bromine used by the gasoline industry. In 1981 only 40 percent of domestic production was consumed as ethylene dibromide.

Other bromine uses, however, have increased; most of this bromine is converted into organic or inorganic compounds. Although the demand for bromine in liquid form was lim-

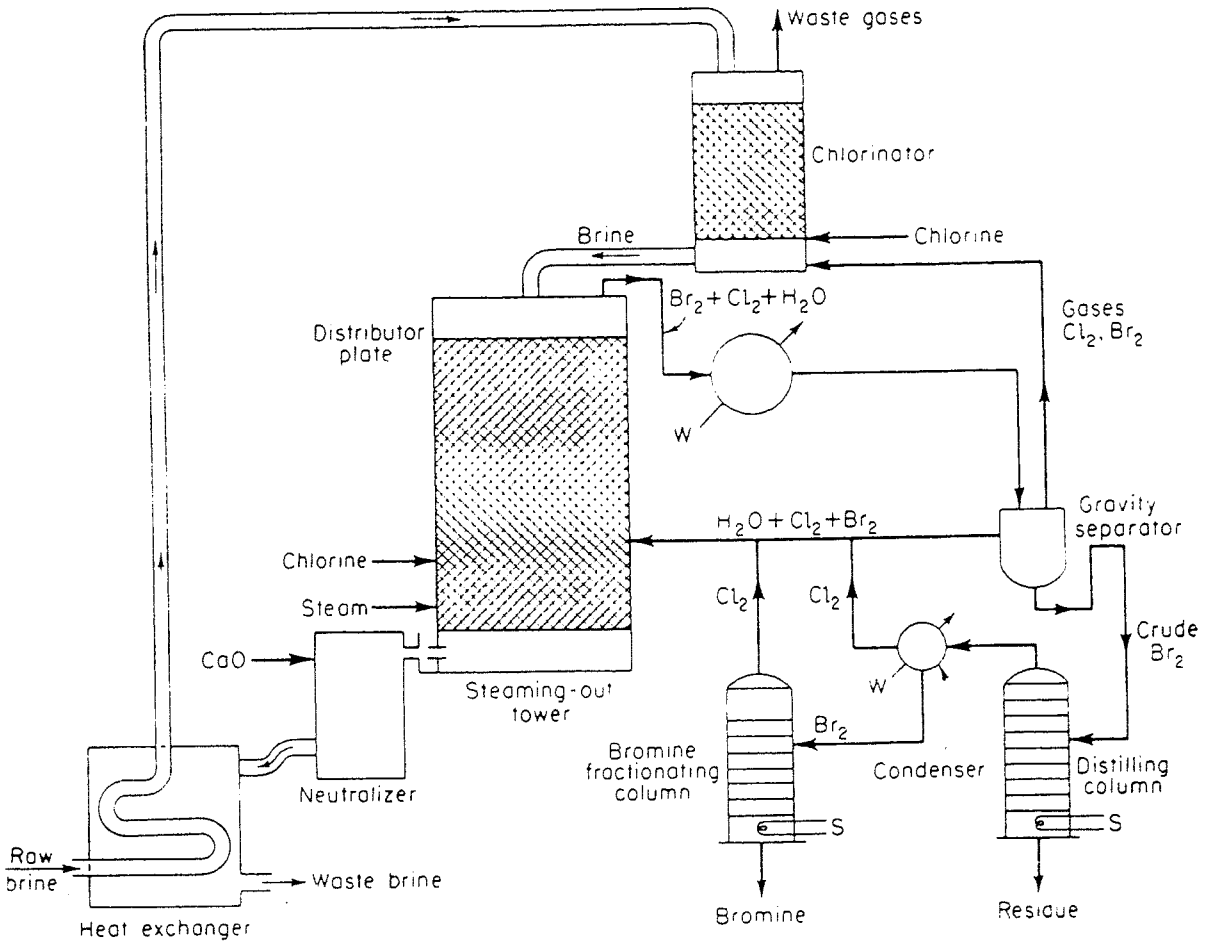

Fig. 5 .3. Steaming-out process for bromine manufacture

ited mostly to laboratory reagents and small specialty uses, there is current interest in its use in swimming pools. Less than 1 ppm of bromine sterilizes the water without eye irritation or objectionable odor. Among the major inorganic compounds are alkali bromides, which are widely employed in photography and as comparatively safe sedatives in medicine. Metallic bromides are used for completion fluids in oil drilling muds and now account for nearly 20 percent of bromine production.

Hydrobromic acid resembles hydrochloric acid but is a more effective solvent for ore minerals, i.e., it has a higher boiling point and stronger reducing action. Methyl bromide (used as an insecticide, rodenticide, and methylating agent) and bromoindigo dyes are important organic compounds. Both methyl bromide and ethylene dibromide are finding growing use as soil and seed fumigants. Ethyl bromide is employed mainly as an ethylating agent in the synthesis of pharmaceuticals (Chap. 40). Bromine is also employed in the preparation of dyes, disinfectants, flameproofing agents, and fire-extinguishing compounds. Flame retardants have been the biggest gainers among the newer uses. As flame-retardant standards become more strict, bromine products gain an increasing share of the market. In 1981 25 percent of bromine was used to produce flame retardants (Chap. 1). A promising new use is in the automobile sealed-beam headlight, which uses a bromine- or iodine-plus-tungsten element in an all-plastic unit. The halogen bulb emits a brigher, whiter light and has a 25 percent greater effective visibility distance than the usual all-glass unit.[5] Prior to World War I, Germany supplied approximately three-quarters of the total world production (1125 t).[5a] By 1929 the

[5] *Mater. Eng.* 92 (5) 36 (1980).

[5a] t = 1000 kg.

total U.S. production was 2886 t plus 7.65 t was imported. Since 1938 no imports have been received. In 1952, 70,290 t (value $30 million) was produced in this country, and by 1981 approximately 170,000 t was produced. The price of bromine in May, 1982 was 55 to 66 cents per kilogram in bulk and $1.90 per kilogram in drums. The United States is the world's largest producer and Israel is second, followed by the United Kingdom and West Germany.

MANUFACTURE. In the United States the chief raw material is seawater, in which bromine occurs in concentrations of 60 to 70 ppm. It is also manufactured from natural brines, where its concentration may be as high as 1300 ppm. In Germany it is produced from waste liquors resulting from the extraction of potash salts from the Stassfurt carnallite deposits, formerly the world's chief source of bromine. Various other countries have the following sources. Italy extracts bromine from one of its largest inland lakes; the U.S.S.R., from the water of Saksky Lake in Crimea; France, from deposits in Alsace; and Israel, from the Dead Sea, the richest source known.

Bromine from Seawater.[6] A process was worked out for the removal of a small quantity of bromine by air-blowing it out of chlorinated seawater according to the equation

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2\uparrow$$

Manufacture from Salt Brines.[7] In ocean water, where the concentration of bromine is relatively dilute, air has proved to be the most economical blowing-out agent. However, in the treatment of relatively rich bromine sources such as brines, *steaming out* the bromine vapor is the more satisfactory (Fig. 5.3). The original steaming-out process was developed by the Germans for processing the Stassfurt deposits, and with modifications is still used there, as well as in Israel and in this country. This process involves preheating the brine to 90°C in a heat exchanger and passing it down a chlorinator tower. After partial chlorination, the brine flows into a steaming-out tower, where steam is injected at the bottom and the remaining chlorine is introduced. The halogen-containing vapor is condensed and gravity-separated. The top water-halogen layer is returned to the steaming-out tower, and the crude halogen (predominantly bromine) bottom layer is separated and purified. *Crude bromine* from any of the foregoing processes can be purified by redistillation or by passing the vapors over iron filings which hold back the chlorine impurity. Alkali bromides account for an important proportion of the bromine produced. They cannot be made by the action of caustic soda on bromine, since hypobromites and bromates are produced also. The van der Meulen process involves treating bromine with potassium carbonate in the presence of ammonia.

$$3K_2CO_3 + 3Br_2 + 2NH_3 \rightarrow 6KBr + N_2 + 3CO_2 + 3H_2O$$

IODINE

HISTORICAL AND RAW MATERIALS. It was in 1811 that Courtois, a saltpeter manufacturer of Paris, obtained a beautiful violet iodine vapor from the mother liquors left from the recrystallization of certain salts. Iodine was later found to exist almost universally in nature. It is present as iodates (0.05 to 0.15%) in the Chilean nitrate deposits. It occurs in seawater, from

[6]See CPI 2 for description; *Chem. Met. Eng.* **46** 771 (1939); ECT, 3d ed., vol. 4, 1978, p. 226.

[7]For flowchart, see ECT, 2d ed., vol. 3, 1964, p. 760.

which certain seaweeds extract and concentrate it within their cells. Iodine has been made from these weeds by the kelp-burning process,[8] which has been practiced for years in Scotland, Norway, Normandy, and Japan. The present sources of the element, as far as the United States is concerned, however, are the nitrate fields of Chile, brine wells in Michigan, Oklahoma, and Japan, involving a total consumption of about 3900 t/year.

USES AND ECONOMICS. In the United States all but 9 percent of the iodine used is converted directly to chemical compounds.[9] The single largest use, 41 percent of the total, is for organic compounds; 21 percent is used for potassium iodide, 9 percent for sodium iodide, and 20 percent for other inorganic compounds. Iodine is used as a catalyst in the chlorination of organic compounds and in analytical chemistry for determination of the so-called *iodine numbers* of oils. Iodine for medicinal, photographic, and pharmaceutical purposes is usually in the form of alkali iodides, prepared through the agency of ferrous iodide. In addition to the above, the element is also employed in the manufacture of certain dyes and as a germicide. Simple iodine derivatives of hydrocarbons, such as iodoform, have an antiseptic action. Organic compounds containing iodine have been used as rubber emulsifiers, chemical antioxidants, and dyes and pigments. For years, Chilean-produced iodine dominated the market and controlled the price, which was set at $10 per kilogram. Upon development of the iodine from oil well brines in the southwestern United States, the price of iodine was reduced to approximately $4.80 per kilogram. Japan has recently become the world's largest iodine producer. In 1971 Japan produced more than three times the amount produced by Chile, and in 1980 over 50 percent of the world's total production. The United States produces less than 30 percent of the amount it uses. The price in 1981 was $15.90 per kilogram. Five of the 18 iodine manufacturing plants in Japan have been built since 1970. Ecological problems may seriously affect their long-term output as ground control and waste disposal regulations become more strict, but at least one of the companies has plants that satisfy environmental requirements.

FLUORINE AND FLUOROCHEMICALS

Fluorine, a pale greenish-yellow gas of the halogen family, is the most chemically active nonmetal element. It occurs in combined form and is second only to chlorine in abundance among the halogens. The chief fluorine-containing minerals of commercial significance are fluorspar, fluorapatite (see superphosphates), and cryolite.

HISTORICAL. Fluorine was discovered by Scheele in 1771 but it was not until 1886 that it was isolated by H. Moissan, after more than 75 years of intensive effort by many experimenters. The Freon refrigerants developed in 1930 fostered the commercial development of anhydrous hydrofluoric acid and stimulated the growth of this new industry, which came into its own at the beginning of World War II,[10] largely because of the demands for UF_6 for isotope separation and for Freons.

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[8]Dyson, Chemistry and Chemotherapy of Iodine and Its Derivatives, *Chem. Age* 22 362 (1930).

[9]*Minerals Yearbook 1980*, vol. 1, Dept. of the Interior, 1981, p. 937; *Chem. Week* 127 (20) 44 (1980); *Chem. Eng. News* 60 (24) 12 (1982).

[10]Finger, Recent Advances in Fluorine Chemistry, *J. Chem. Ed.* 28 49 (1951); ECT, 3d ed., vol. 10, 1980, p. 630.

USES AND ECONOMICS. Elemental fluorine is costly and has comparatively limited usage. The element is employed in making sulfur hexafluoride (SF_6) for high-voltage insulation and for uranium hexafluoride. Fluorine is used directly or combined with higher metals (cobalt, silver, cerium, etc.) and halogens (chlorine and bromine) for organic fluorinations and the growing production of fluorocarbons. The largest production of fluorine compounds is that of hydrofluoric acid (anhydrous and aqueous), used in making "alkylate" for gasoline manufacture and Freon for refrigerants and aerosol cans. It is also employed in the preparation of inorganic fluorides, elemental fluorine, and many organic fluorine- and non-fluorine-containing compounds. Aqueous hydrogen fluoride is used in the glass, metal, and petroleum industries and in the manufacture of many inorganic and acid fluorides. Three of the most unusual plastics known (Chap. 34) are Teflon, a polymerization product of tetrafluorethylene, and Kel F and Fluorothene, products formed by the polymerization of chlorofluorethylenes.

The production of hydrofluoric acid has increased rapidly to keep pace with these varied and expanding uses.[11] In 1939, 6678 t was produced, in 1963, 117,045 t, and in 1981, 328.000 t. Hydrofluoric acid sells for $1.23 per kilogram in the anhydrous form (in tank cars) and $1.58 per kilogram as a 70 percent solution (in drums). About 42 percent of the hydrogen fluoride produced is used to prepare fluorocarbons, and one-third of the total goes to the aluminum industry, where synthetic cryolite, sodium aluminum fluoride, is a major constituent of the electrolyte. It is also consumed in the melting and refining of secondary aluminum. Other uses of hydrofluoric acid are found in the metals and petroleum industries.

MANUFACTURE. *Fluorine gas* is generated by the electrolysis of KHF_2[12] under varying conditions of temperature and electrolyte composition.

Both *aqueous* and *anhydrous hydrofluoric acid* are prepared in heated kilns by the following endothermic reaction:

$$CaF_2 \text{ (fluorspar)} + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

The hot, gaseous hydrogen fluoride is either absorbed in water or liquefied; refrigeration is employed to obtain the anhydrous product needed for fluorocarbon manufacture and other uses. Although hydrofluoric acid is corrosive, concentrations of 60% and above can be handled in steel at lower temperatures; lead, carbon, and special alloys are also used in the process equipment.

FLUOROCARBONS. These are compounds of carbon, fluorine, and chlorine with little or no hydrogen. Fluorocarbons containing two or more fluorines on a carbon atom are characterized by extreme chemical inertness and stability. Their volatility and density are greater than those of the corresponding hydrocarbons. More than 360×10^6 kg of fluorocarbons was produced in 1980: Refrigerants consumed 46 percent; foam blowing agents, 20 percent; solvents, 16 percent; fluoropolymers, 7 percent; and aerosol propellants less than 1 percent.[13]

Prior to 1974 aerosol propellants were the major (52 percent) end use market of fluorocarbons. In 1974 scientists at the University of California at Irvine, and at the University of Michigan, hypothesized that chlorofluorocarbons used as aerosol propellants would eventually find their way to the upper atmosphere. There they would react with the ozone layer that

[11]*Chem. Mark. Rep.* July 20, 1981.

[12]ECT, 3d ed., vol. 10, 1980, p. 644. Flow diagrams for fluorine production and liquefaction.

[13]*Chem. Mark. Rep.* Aug. 24, 1981.

shields the earth from ultraviolet rays. A reduction in the ozone layer could allow more ultraviolet rays to reach the earth, causing a change in global weather patterns and an increase in skin cancer. This hypothesis resulted in bills being introduced in Congress and in several state legislatures to prohibit the manufacture, sale, and use of aerosols containing chlorofluorocarbons. In 1975 Oregon passed such a bill. Study committees were formed to determine the actual effect of these compounds on the ozone layer, but the "scare" caused a sharp decrease in the number of aerosol containers filled with fluorocarbons in 1976 as compared with 1974. In 1978 the Environmental Protection Agency banned the use in aerosol containers. However, only three other countries have banned fluorocarbon use for this purpose. In addition, new studies are casting doubt upon the original assumption that fluorocarbons alone are responsible for depletion of the ozone layer of the earth's atmosphere.[14]

The major use for refrigerants takes 46 percent of the production, and the remainder goes into over 100 different important applications, including plastics, films, elastomers, lubricants, textile-treating agents, solvents, and fire extinguisher products. Fluorocarbons are made from chlorinated hydrocarbons by reacting them with anhydrous hydrogen fluoride, using an antimony pentachloride catalyst. The fluorocarbons trichlorofluoromethane, dichlorodifluoromethane, and chlorodifluoromethane compose 90 percent of fluorocarbon production.

$$CCl_4 + HF \xrightarrow{SbCl_5} CCl_3F + HCl$$

$$CCl_4 + 2HF \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl$$

Difluoromonochloromethane is made by substituting chloroform for the carbon tetrachloride:

$$CHCl_3 + 2HF \xrightarrow{SbCl_5} CHClF_2 + 2HCl$$

The fluorocarbon process shown in Fig. 20.4 may be divided into the following coordinated sequences:

Anhydrous hydrogen fluoride and carbon tetrachloride (or chloroform) are bubbled through molten antimony pentachloride catalyst. These reactions are slightly endothermic and take place in a steam-jacketed atmospheric pressure reactor at 65 to 95°C.

The gaseous mixture of fluorocarbon and unreacted chlorocarbon is distilled to separate and recycle the chlorocarbon to the reaction.

Waste hydrogen chloride is removed by water absorption.

The last traces of hydrogen chloride and chlorine are removed in a caustic scrubbing tower.

FLUOROSILICATES OR SILICOFLUORIDES. An important potential source of fluorine compounds is phosphate rock which, in processing, yields recoverable fluorine by-products. In 1962 Stauffer Chemical announced plans for the production of hydrogen fluoride from this source.[15] The wet process for superphosphates (Chap. 1) evolves a toxic gaseous mixture of

[14]Fluorocarbons Are an Issue Again, *Chem. Bus.* June 1, 1981; *Chem. Week* 130 (5) 16 (1982).

[15]See Chap. 16, Phosphorus Industries.

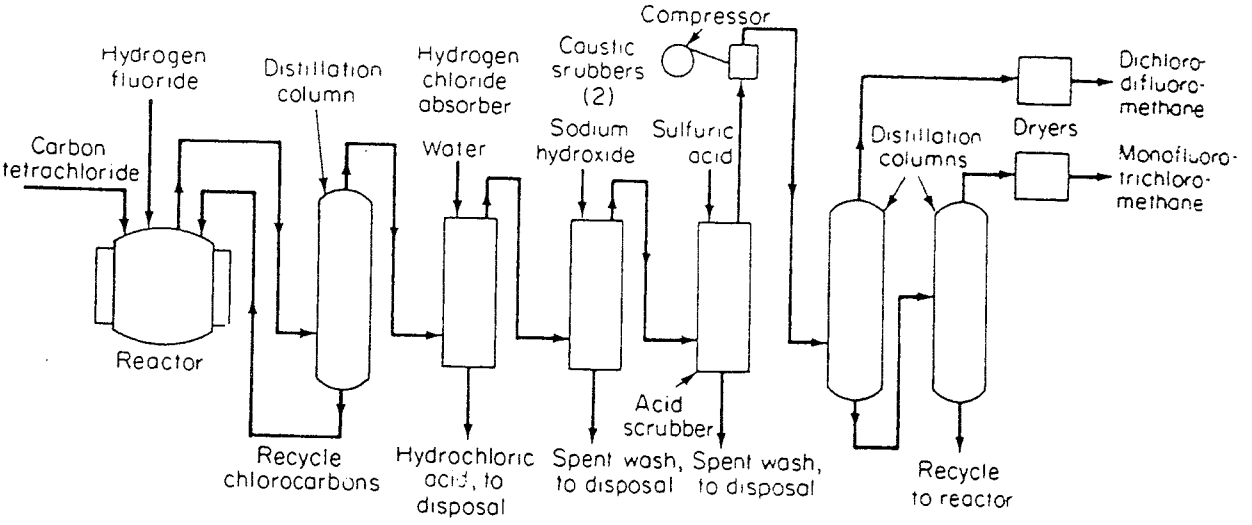


Fig. 5.4. Fluorocarbon production. [*Chem. Eng.* 72 *(2) 93 (1965).*]

fluorine compounds, predominantly silicon tetrafluoride, hydrofluoric acid, and fluorosilicic acid (H_2SiF_6). This mixture is passed through water-absorption towers, yielding fluorosilicic acid and a silica precipitate. The H_2SiF_6 liquor is concentrated to commercial strengths (generally 30 to 35%) by recycling or distillation. An important use for this acid is in the fluoridation of municipal water supplies and also in the brewing industry as a disinfectant for copper and brass vessels. It is also employed as a preservative, in electroplating, as a concrete hardener, and in the manufacture of silicofluoride salts. The most common salt, *sodium silicofluoride* (Na_2SiF_6), is prepared by the reaction of sodium chloride or soda ash on the acid. It is used as an insecticide, laundry sour, fluxing and opacifying agent, and protective agent in the casting of light metals. Other salts such as ammonium, magnesium, zinc, copper, and barium are also prepared by neutralization and find many uses in industry.

ALUMINA

USES AND ECONOMICS. Large quantities of alumina are produced yearly for the manufacture of metallic aluminum (Chap. 14). In 1980, 90 percent of the raw material, *bauxite*, was obtained from foreign sources.[16] Jamaica, Haiti, the Dominican Republic, Surinam, Guyana, Guinea, and Australia are the countries from which the United States imports this bauxite. Total consumption was 15.6×10^6 t, about 96 percent of this going to alumina production; smaller uses include abrasives, chemical manufacture, refractories, and ceramic fibers.

MANUFACTURE. Figure 5.5 shows the essential procedure in the production of alumina, which may be divided into the following steps:

Bauxite, a mineral containing about 55% aluminum oxide and less than 7% silica, is crushed and wet-ground to 100-mesh.

The finely divided bauxite is dissolved under pressure and heat in Bayer digesters with concentrated spent caustic soda solution from a previous cycle and sufficient lime and soda

[16] *Minerals Yearbook 1980*, vol. 1, Dept. of the Interior, 1981, p. 113.

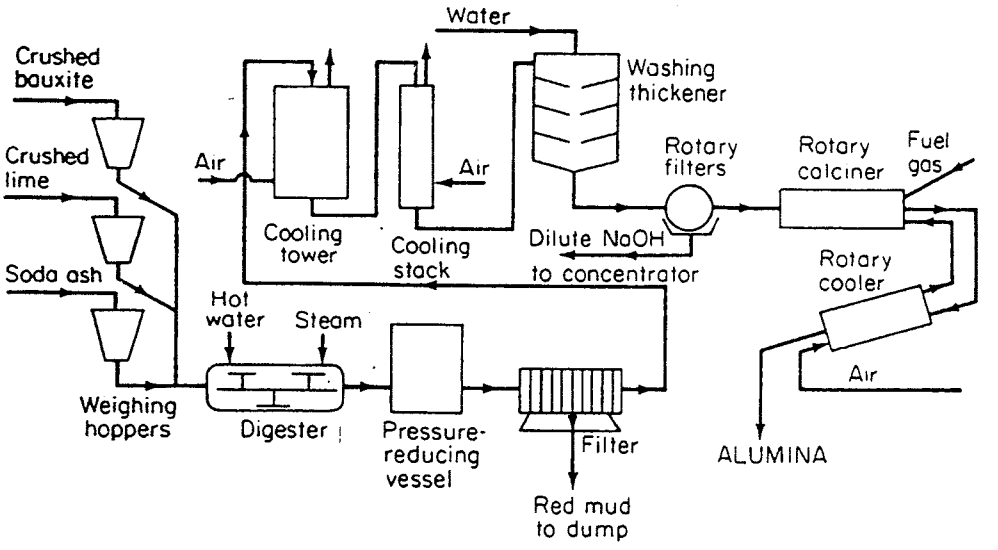


Fig. 5 .5. Refining of aluminum.

ash. Sodium aluminate is formed, and the dissolved silica is precipitated as sodium aluminum silicate.

The undissolved residue (red mud) is separated from the alumina solution by filtration and washing and sent to recovery. Thickeners and Kelly or drum filters are used.

The filtered solution of sodium aluminate is hydrolyzed to precipitated aluminum hydroxide by cooling.

The precipitate is filtered from the liquor and washed.

The aluminum hydroxide is calcined by heating to 980°C in a rotary kiln.

The alumina is cooled and shipped to reduction plants.

The dilute caustic soda filtered from the aluminum hydroxide is concentrated for reuse.

The red mud may be reworked for recovery of additional amounts of alumina.

Several other processes for producing alumina based on ores other than bauxite have been announced. A Mexican process (called the U.G. process) uses alunite, a hydrous sulfate of aluminum and potassium. It is claimed to be capable of producing 99% pure alumina from alunite containing only 10 to 15% alumina, compared with bauxite which assays 50% alumina. The alunite is crushed, dehydroxylated by heating to 750°C, ground, and treated with aqueous ammonia. Filtration removes the alumina hydrate, and potassium and aluminum sulfates are recovered from the filtrate and sold as fertilizer. The alumina hydrate is treated with sulfur dioxide gas, and the resulting aluminum sulfate converted to alumina by heating in a kiln.[17]

The French Pechiney-Ugine Kuhlmann process treats clays and shales with concentrated sulfuric acid. Hydrochloric acid is added during the crystallization step to form aluminum chloride which crystallizes readily. Much raw material must be handled, because the clays and shales have a lower alumina content than bauxite.[18]

Other methods involve the treatment of clays with nitric acid (Bureau of Mines) and the continuous electrolysis of aluminum chloride (Alcoa).

[17]Parkinson, Alumina From Alunite, *Eng. Min. J.* **175** (8) 75 (1974).

[18]Alumina Producers Look to Alternate Raw Materials, *Chem. Eng.* **81** (9) 98 (1974); Patterson, Aluminum from Bauxite, Are There Alternatives? *Am. Sci.* **65** 345 (1977); Barclay and Peters, New Sources of Alumina, *Min. Cong. J.* **62** (6) 29 (1976).

ALUMINUM SULFATE AND ALUMS

The manufacture of alums entails just one step additional to the aluminum sulfate process. This, along with the fact that the uses of aluminum sulfate and alums are similar and the compounds are largely interchangeable, justifies their concurrent discussion. The term *alum* has been very loosely applied. A true alum is a double sulfate of aluminum or chromium and a monovalent metal (or a radical, such as ammonium). Aluminum sulfate is very important industrially and, although it is not a double sulfate, it is often called either alum or papermakers' alum. Alum has been known since ancient times. The writings of the Egyptians mention its use as a mordant for madder and in certain medical preparations. The Romans employed it to fireproof their siege machines and probably prepared it from alunite, $K_2Al_6(OH)_{12}(SO_4)_4$, which is plentiful in Italy.

USES AND ECONOMICS. Alums are used in water treatment and sometimes in dyeing. They have been replaced to a large extent in these applications by aluminum sulfate, which has a greater alumina equivalent per unit weight. Pharmaceutically, aluminum sulfate is employed in dilute solution as a mild astringent and antiseptic for the skin. The most important single application of it is in clarifying water, more than half of the total amount manufactured being so consumed. Sodium aluminate, which is basic, is sometimes used with aluminum sulfate, which is acid, to produce the aluminum hydroxide floc:

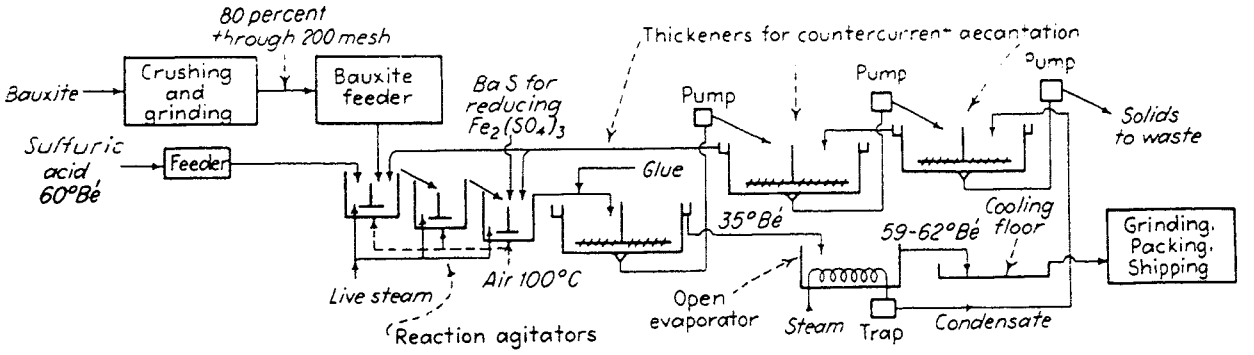
$$6NaAlO_2 + Al_2(SO_4)_3 + 12H_2O \rightarrow 8Al(OH)_3 + 3Na_2SO_4$$

Second in importance is the application of aluminum sulfate in the sizing of paper. It reacts with sodium resinate to give the insoluble aluminum resinate. For the sizing of paper, aluminum sulfate must be free from ferric iron, or the paper will be discolored. The ferrous ions do not harm, since they form a soluble, practically colorless resinate, which, however, represents a loss of resinate. A small amount of aluminum sulfate is consumed by the dye industry as a mordant. Other uses include chemical manufacturing, concrete modification, pharmaceutical preparations, soaps and greases, fire extinguishing solutions, tanning, and cellulosic insulation. Soda alum, or aluminum sulfate, is used in some baking powders. In 1981, 1,085,000 t of commercial aluminum sulfate was produced.[19]

MANUFACTURE. Practically all alums and aluminum sulfate are now made from bauxite by reaction with 60°Bé sulfuric acid. However, potash alum was first prepared from alunite by the ancients. Other possible sources of alums are shales and other alumina-bearing materials such as clay. Figure 5.6 illustrates the manufacture of aluminum sulfate.[20] The bauxite is ground until 80 percent passes 200 mesh; next it is conveyed to storage bins. The reaction occurs in lead-lined steel tanks, where the reactants are thoroughly mixed and heated with the aid of agitators and live steam. These reactors are operated in series. Into the last reactor barium sulfide is added in the form of black ash to reduce ferric sulfate to the ferrous state and to precipitate the iron. The mixture from the reactors is sent through a series of thickeners, operated countercurrently, which remove undissolved matter and thoroughly wash the

[19]*Chem. Eng. News* 60 (24) 33 (1982).

[20]*Chem. Eng. Prog.* 70 (1) 55 (1974) (alum flowchart of Allied Chemical Corp.); ECT, 3d ed., vol. 2, 1978, p. 218.



In order to produce 1 t of 17% Al_2O_3 "alum," the following materials and utilities are required:

Bauxite (55% Al_2O_3)	338 kg	Coal (steam)	380 kg
H_2SO_4 (60°Bé)	575 kg	Electricity	115 MJ
Black ash (70% BaS)	6.6 kg	Direct labor	1.6 work-h
Flake glue	0.2 kg		

Fig. 5 .6. Manufacture of aluminum sulfate by the Dorr process. NOTE: A common variation of this flow sheet is to use a battery of combined reaction and settling tanks instead of agitators and thickeners.

waste so that, when discarded, it will contain practically no alum. The clarified aluminum sulfate solution is concentrated in an open, steam-coil heated evaporator from 35 to 59 or 62°Bé. The concentrated liquor is poured into flat pans, where it is cooled and completely solidified. The solid cake is broken and ground to size for shipping. Another slightly modified procedure uses, instead of reactors and thickeners, combined reaction and settling tanks. The Dalecarlia rapid-sand filter plant, which supplies water to Washington, D.C., makes its own filter alum. In this case concentration of liquor would be an unnecessary expense; therefore the aluminum sulfate is made and used in a water solution. To make the various true alums, it is necessary only to add the sulfate of the monovalent metal to the dilute aluminum sulfate solution in the proper amount. Concentration of the mixed solution, followed by cooling, yields alum crystals.

ALUMINUM CHLORIDE

Aluminum chloride is a white solid when pure. On heating it sublimes and, in the presence of moisture, anhydrous aluminum chloride partly decomposes with the evolution of hydrogen chloride. This salt was first prepared in 1825 by Oersted, who passed chlorine over a mixture of alumina and carbon and condensed the vapors of the aluminum chloride formed. Essentially the same process is used today in the commercial preparation of aluminum chloride. The price in 1913 was $3.30/kg and the present price is $1.00/kg in carload lots.

USES. Since modern methods of manufacture have reduced the price of aluminum chloride, it has found application in the petroleum industries and various phases of organic chemistry technology. Aluminum chloride is a catalyst in the alkylation of paraffins and aromatic hydrocarbons by olefins and also in the formation of complex ketones, aldehydes, and carboxylic acid derivatives. In 1980, 25,000 t of anhydrous aluminum chloride was manufactured. Anhydrous aluminum chloride is manufactured primarily by the reaction of chlorine vapor on molten aluminum.[21] Chlorine is fed in below the surface of the aluminum, and the product

sublimes and is collected by condensing. These air-cooled condensers are thin-walled, vertical steel cylinders with conical bottoms. Aluminum chloride crystals form on the condenser walls and are periodically removed, crushed, screened, and packaged in steel containers.

COPPER SALTS

Copper sulfate[22] is the most important compound of copper, and more than 29000 t was produced in 1976. Commonly known as *blue vitriol*, it is prepared by the action of sulfuric acid on cupric oxide or sulfide ores. Its poisonous nature is utilized in the fungicide Bordeaux mixture, which is formed upon mixing copper sulfate solution with milk of lime. Copper sulfate is added to water reservoirs occasionally to kill algae. It is employed in electroplating and finds minor applications as a mordant, germicide, and agent in engraving. Certain copper compounds are added to antifouling paints used on ship bottoms.

MOLYBDENUM COMPOUNDS

Although the largest use for molybdenum lies in metallurgy, chemical applications make up a rapidly growing segment of diversified uses. Approximately 10 percent of the total molybdenum production of over 51,000 t/year goes into compounds.[23] Molybdenum disulfide is dispersed in greases and oils for lubrication; in volatile carriers it is used to form dry coatings of lubricant. Sodium molybdate is an especially effective corrosion inhibitor on aluminum surfaces and is dissolved in cooling solutions to protect aluminum motor blocks in automobiles.[24] Molybdenum salts used as catalysts include cobalt molybdate for hydrogen treatment of petroleum stocks for desulfurization, and phosphomolybdates to promote oxidation. Compounds used for dyes are sodium, potassium, and ammonium molybdates. With basic dyes, phosphomolybdic acid is employed. The pigment known as *molybdenum orange* is a mixed crystal of lead chromate and lead molybdate. Sodium molybdate, or molybdic oxide, is added to fertilizers as a beneficial trace element. Zinc and calcium molybdate serve as inhibitory pigments in protective coatings and paint for metals subjected to a corrosive atmosphere. Compounds used to produce better adherence of enamels are molybdenum trioxide and ammonium, sodium, calcium, barium, and lead molybdates. The mineral raw material is molybdenite, which, by roasting, furnishes a technical grade of molybdenum trioxide of 80 to 90% purity.

BARIUM SALTS

The most common naturally occurring barium compounds are the mineral carbonate, or witherite, which is fairly abundant in England, and the sulfate, or barite, which is common in certain sections of the United States. The most important domestic source of barite is Nevada, but there are mines in many other states. West Germany has become the major

[22]ECT, 3d ed., vol. 7, 1979, p. 97.

[23]*Minerals Yearbook 1980*, vol. 1, Dept. of Interior, 1981, p. 103.

[24]Vukasovich, Sodium Molybdate Corrosion Inhibition, *Lubr. Eng.* 36 (12) 709 (1980); *Mod. Paint Coat.* 70 (2) 45 (1980).

foreign supplier of barium carbonate to the U.S. market. A new source is China, and this country may become a major supplier in the future. Domestic production in 1980 was 2×10^6 t and imports were 1.7×10^6 t.

USES.[25] The applications of barium compounds are varied and important. Each year over 3×10^6 t of barite is consumed. Over 90 percent is used for oil drilling muds. *Barium carbonate* is sometimes employed as a neutralizing agent for sulfuric acid and, because both barium carbonate and barium sulfate are insoluble, no contaminating barium ions are introduced. The foregoing application is found in the synthetic dyestuff industry. The glass industry uses 28 percent of the barium carbonate produced, and brick and clay producers, 33 percent. When barium carbonate is added to the clay used in making bricks, it immobilizes the calcium sulfate and prevents it from migrating to the surface of the bricks and producing a whitish surface discoloration. Miscellaneous uses include TV picture tubes and as a flux for ceramics. Witherite is used chiefly to prepare other compounds. *Barium sulfate* is a useful white pigment (Chap. 24), particularly in the precipitated form, blanc fixe. It is used as a filler for paper, rubber, linoleum, and oilcloth. Because of its opacity to x-rays, barium sulfate, in a purified form, is important in contour photographs of the digestive tract. The paint industry is the largest single consumer of barium compounds. Barium sulfide and zinc sulfate solutions are mixed to give a precipitate of barium sulfate and zinc sulfide, which is given a heat treatment to yield the cheap but good pigment *lithopone*, as described in Chap. 24. Barium chlorate and nitrate are used in pyrotechnics to impart a green flame. Barium chloride is applied where a soluble barium compound is needed. Barium saccharate is used by a large beet-sugar company in recovering sugar from discarded molasses (Chap. 30).

MANUFACTURE. The preparation of soluble barium salts is simple where witherite is available. The only steps necessary are treatment with the proper acid, filtration to remove insoluble impurities, and crystallization of the salt. Since there is little witherite in the United States, barium salts are prepared from barite. The high-temperature reduction of barium sulfate with coke yields the water-soluble barium sulfide, which is subsequently leached out. The treatment of barium sulfide with the proper chemical yields the desired barium salt. Purification of the product is complicated by the impurities introduced in the coke. Pure barium carbonate and barium sulfate are made by precipitation from solutions of water-soluble barium salts. Much barite is ground, acid-washed, lixiviated, and dried to produce a cheap pigment or paper or rubber filler, or changed to blanc fixe.

STRONTIUM SALTS

Uses of strontium salts are small with respect to tonnage consumed but they are important; they include red-flame pyrotechnic compositions, such as truck signal flares and railroad "fusees," tracer bullets, military signal flares, and ceramic permanent magnets. Strontium carbonate is widely used as an x-ray screening agent in television picture-tube face plate glass and has no commercial alternative. Low-grade strontium deposits are available in this country, but are not currently in use; high-grade celestite is imported from Mexico and the United

[25] *Minerals Yearbook 1980*, vol. 1, Dept. of the Interior, 1981 p. 103; *Chem. Week* **129** (6) 26 (1981).

Kingdom. This ore (strontium sulfate) is finely ground and converted to the carbonate by boiling with 10% sodium carbonate solution, giving almost a quantitative yield:

$$SrSO_4 + Na_2CO_3 \rightarrow SrCO_3 + Na_2SO_4$$

From reaction of the strontium carbonate with appropriate acids, the various salts result.

LITHIUM SALTS

During World War II lithium hydride was reacted with seawater to produce a convenient lightweight source of hydrogen for the inflation of air-sea rescue equipment. Interest in lithium compounds grew from 1954 to 1960, when the Atomic Energy Commission (AEC) bought vast quantities of lithium hydroxide, presumably for use in the production of hydrogen bombs.[26] Termination of these contracts left a substantial excess, which in turn has fostered new commercial uses. The largest known lithium ore reserve in the world is in the King's Mountain district of North Carolina. Currently a large part of the free world's output of lithium oxide comes from this source as spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$). There are only two producers of lithium and lithium salts in the United States: Foote Mineral Co. and Lithium Corp. of America. Foote produces lithium from the ore in North Carolina and from subsurface brines in Nevada. All of Lithium Corp. production is from North Carolina sources. In 1980 the U.S. produced 6480 t of lithium metal equivalent and exported 33 percent of the total.[27]

USES. Lithium carbonate, the most widely used of the compounds, is employed in the production of lithium metal and frits and enamels. Together with lithium fluoride, it serves as an additive for cryolite in the electrolytic pot line production of primary aluminum. The addition of 2.5 to 3.5% of lithium carbonate to the electrolytic bath causes the formation of a eutectic mixture that lowers the bath temperature, power consumption, and rate of volatilization of fluoride salts. This use accounts for 33 percent of the lithium produced in the United States.[28] Lithium-base greases, often the stearate, are a large outlet. These lubricants are efficient over the extremely wide temperature range −51° to 160°C. Lithium hydroxide is a component of the electrolyte in alkaline storage batteries and is employed in the removal of carbon dioxide in submarines and space capsules. Lithium bromide brine is used for air conditioning and dehumidification. The hypochlorite is a dry bleach used in commercial and home laundries. Lithium chloride is in demand for low-temperature batteries and for aluminum brazing. Other lithium-compound uses include catalysts, glass manufacture, and of course nuclear energy. A newer use for lithium carbonate is as a drug to treat manic depression. The Food and Drug Administration (FDA) approved its use for treating mind disorders in 1970.[29]

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[26]The lithium hydroxide for sale by AEC is devoid of lithium-6 isotope.

[27]ECT, 3d ed., vol. 14, 1981, p. 450; *Minerals Yearbook 1980*, vol. 1, Dept. of the Interior, 1981, p. 519.

[28]Stinson, Lithium Producers Gear Up for Bright Future, *Chem. Eng. News* **59** (43) 11 (1981); *Chem. Eng. News* **59** (42) 10 (1981); *Chem. Week* **128** (10) 19 (1981).

[29]*Chem. Week* **110** (10) 41 (1972).

MANUFACTURE. Since spodumene is by far the most important ore, the manufacture of lithium carbonate from it is presented. Spodumene ore (beneficiated to 3 to 5% Li_2O) is converted from the alpha form to the beta form by heating to over 1000°C. The alpha form is not attacked by hot H_2SO_4. The beta form is treated as follows:

$$\text{excess } Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + H_2SO_4 \xrightarrow[\text{rotary kiln}]{250°\text{-}300°C} H_2O \cdot Al_2O_3 \cdot 4SiO_2 + Li_2SO_4$$

The water-soluble lithium sulfate is leached out and reacted with sodium carbonate to yield lithium carbonate. Various salts are derived from the carbonate as follows:

$$Li_2CO_3 + Ca(OH)_2 + 2H_2O \rightarrow CaCO_3 + 2LiOH \cdot H_2O \xrightarrow{\Delta} 2LiOH$$

$$Li_2CO_3 + 2HCl \rightarrow H_2O + CO_2 + 2LiCl(soln) \xrightarrow{\Delta} 2LiCl(anyhd)$$

$$2LiCl(anhyd) \xrightarrow{\text{electrolysis}} 2Li + Cl_2\uparrow \xrightarrow{H_2} 2LiH \xrightarrow{2NH_3} 2LiNH_2 + 2H_2\uparrow$$

BORON COMPOUNDS

The important naturally occurring ores of boron have been colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), tincal ($Na_2B_4O_7 \cdot 10H_2O$), and boracite ($2Mg_3B_8O_{15} \cdot MgCl_2$). However, boron-containing brines and kernite, or rasorite ($Na_2B_4O_7 \cdot 4H_2O$), are also sources in the United States.

USES. Borax (tincal), $Na_2B_4O_7 \cdot 10H_2O$, is the most important industrial compound of boron. Table 5 .2 lists the U.S. consumption of boron minerals and compounds. The largest single use is in the manufacture of glass-fiber insulation. Boric acid (H_3BO_4) is a weak acid that finds some use in the manufacture of glazes and enamels for pottery. Its main uses are as a fire

Table 5 .2 U.S. Consumption of Boron Minerals and Compounds (metric tons of boron oxide content)

End Use	1980	1981
Glass-fiber insulation	81,265	94,082
Fire retardants		
Cellulosic insulation	45,632	31,179
Other	1,182	2,545
Textile grade glass fibers	45,814	52,268
Borosilicate glasses	40,732	40,000
Soaps and detergents	24,179	26,452
Enamels, frits, glazes	12,090	10,635
Agriculture	14,271	15,090
Metallurgy	6,000	6,182
Nuclear applications	454	364
Miscellaneous uses	43,905	23,090
Sold to distributors. end use unknown	33,540	36,815
Total consumption*	349,000	338,780

*Data may not add to totals shown because of independent rounding.

SOURCE: *Minerals Yearbook 1981*, vol. 1, Dept. of the Interior, 1982, p. 146

retardant for cellulosic insulation and in the manufacture of borosilicate glasses and textile-grade glass fibers

MANUFACTURE. All of the domestic boron ores and brines that are used commercially in producing boron compounds are in California. Three-quarters of the borates thus produced are from an open pit mine in Kern county. Crude and refined hydrated sodium borates and hydrous boric acid are produced by U.S. Borax and Chemicals Corp. from kernite and tincal mined at Boron, Calif. A new plant (1980) at Boron produces 180,000 t/year of boric acid from kernite. The ore is crushed and blended to a constant B_2O_3 content. The blended ore is fed to the dissolving plant and mixed with hot recycle liquor. Liquor and fine insolubles are fed to a primary thickener. There are four thickener stages operating countercurrently. The strong liquors are crystallized in a continuous vacuum crystallizer.[30]

Kerr-McGee Chemical Corp. uses a process that involves the use of an organic solvent to extract the borax from the Searles Lake brines.[31] See Figs. 2.1 and 2.2.

The boric acid is extracted with kerosene, carrying a patented chelating agent not yet disclosed but probably an aliphatic medium chain length polyol, in a mixer-settler system. In a second mixer-settler system, dilute sulfuric acid strips the borates from the chelate. The aqueous phase with boric acid, potassium sulfate, and sodium sulfate is purified by carbon treatment and evaporated in two evaporator-crystallizers; from the first, pure boric acid is separated, and from the other, a mixture of sodium and potassium sulfates.

RARE-EARTH COMPOUNDS

Chemical elements with atomic number 58 to 71 are so nearly identical in properties that they are separated only with difficulty and are called as a group *rare earths.*[32] The name is a misnomer, since they are neither rare nor earths. Compounds of lanthanum, yttrium, and scandium are often included in this group, as are the actinide rare earths (elements 89 and above). Cerium and thorium are the most important commercially. Although rare earths occur in certain minerals native to the Carolinas, these minerals have not been able to compete with the richer monazite sands found in Brazil and in Travancore-Cochin, India. Preliminary separation is accomplished by the use of jigging, in this case the valuable material is denser than the worthless fraction. The concentrates are leached with hot sulfuric acid of strength greater than 66°Bé, and the rare-earth metal compounds are precipitated by dilution of the sulfuric acid solution. Lanthanum and cerium are separated by fractional crystallization, and the others are separated by liquid-liquid extraction or ion-exchange processes.

Molycorp, Inc. has developed a solvent extraction process for the production of the oxides of lanthanum, cerium, gadolinium, terbium, praesodymium, neodymium, yttrium, and europium in tonnage quantities. The ore, bastnäsite, mined in California, is concentrated by hot-froth flotation and then subjected to solvent extraction.[33]

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[30]*Minerals Yearbook 1980,* vol. 1, Dept. of the Interior, 1981, p. 133.

[31]ECT, 3d ed., vol. 4, 1978, p. 67; Shreve, Organic and Other Non-aqueous Solvents as Processing Media for Making Inorganic Chemicals, *Ind. Eng. Chem.* 49 836 (1957).

[32]*McGraw-Hill Encyclopedia of Science and Technology,* 5th ed., vol. 11, McGraw-Hill, New York, 1982, p. 401.

[33]*Minerals Yearbook 1980,* vol. 1, Dept. of the Interior, 1981, p. 669.

The glass industry is the largest consumer of rare-earth compounds, mostly as oxides for rapid polishing of plate glass, as well as precision optical equipment and eyeglasses. Yttrium and europium oxides are used in ton quantities as phosphors for TV screens. Lesser quantities of compounds are used for coloring, decoloring, and opacifying glass. Other uses are in ultraviolet absorbing glass, in certain high-lead glass with increased radiation stability, in color television tubes, lasers, and x-ray intensifying screens. Fluorides and oxides are consumed in the production of carbon electrodes for arc lighting of high intensity and good color balance. Over 300 t of the rare-earth silicide, known as *misch metal*, was used in high-strength, low-alloy steels in 1980. Thorium is of interest in nuclear reactions.

SODIUM DICHROMATE

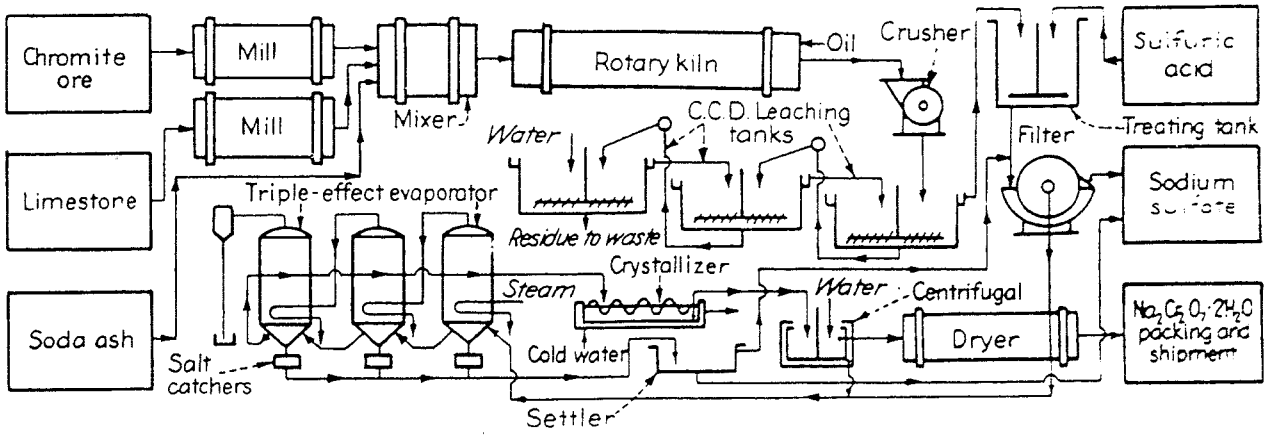
The starting material for the manufacture of sodium dichromate and other chromium compounds is chromite, a chromium iron oxide containing approximately 50% Cr_2O_3, the balance being principally FeO, Al_2O_3, SiO_2, and MgO. There are no high-grade chromite deposits in the United States, and most of the ore used in the chemical industry is imported from the U.S.S.R. Much sodium dichromate is consumed as the starting material for making, by glucose reduction, the solutions of chromium salts employed in chrome leather tanning (Chap. 25) and in chrome mordant dyeing of wool cloth. Certain pigments, such as yellow lead chromate, are manufactured basically from sodium dichromate, as are also green chromium oxides for ceramic pigments. Over half of the chromium enters the metal field as stainless steel and other high-chromium alloys and for chromium plating of other metals, the balance being about equally divided between chrome refractories and chrome chemicals.

The ore is ground to 200-mesh, mixed with ground limestone and soda ash, and roasted at approximately 1200°C in a strongly oxidizing atmosphere. The sintered mass is crushed and leached with hot water to separate the soluble sodium chromate. The solution is treated with enough sulfuric acid to convert the chromate to dichromate, with the resulting formation of sodium sulfate. Most of the sodium sulfate crystallizes in the anhydrous state from the boiling-hot solution during acidification, and the remainder drops out in the evaporators on concentrating the dichromate solution. From the evaporator the hot, saturated dichromate solution is fed to the crystallizer, and then to the centrifuge and dryer (Fig. 5.7).

HYDROGEN PEROXIDE

Hydrogen peroxide is the most widely used peroxide compound. Originally, it was produced by the reaction of barium peroxide and sulfuric acid for use as an antiseptic, but this process and use have been superseded.

USES. Hydrogen peroxide applications include commercial bleaching dye oxidation, the manufacture of organic and peroxide chemicals, and power generation. Bleaching outlets consume more than one-half of the hydrogen peroxide produced. These include bleaching of wood, textile-mill bleaching of practically all wood and cellulosic fibers, as well as of major quantities of synthetics, and paper- and pulp-mill bleaching of groundwood and chemical pulps. The advantage of hydrogen peroxide in bleaching is that it leaves no residue and gen-



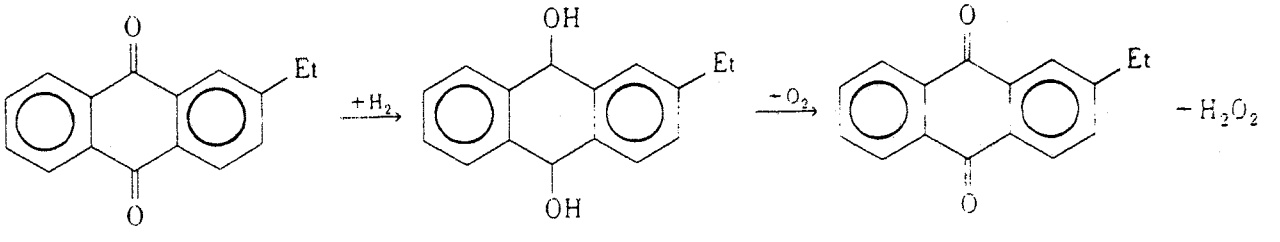
In order to produce 1 t sodium dichromate and 0.66 t anhydrous sodium sulfate, the following materials and utilities are required.

Chromite ore	1.1 t	Fuel oil	0.52 t
Limestone	1.65 t	Steam	3 t
Soda ash	0.88 t	Electricity	1980 MJ
Sulfuric acid, 66°Bé	0.5 t	Direct labor	15 work-h

Fig. 5.7. Flowchart for the manufacture of sodium dichromate from chrome ore.

erally results in an excellent product whiteness, with little or no *deterioration* of the organic matter that is bleached. Organic applications include manufacture of epoxides and glycols from unsaturated petroleum hydrocarbons, terpenes, and natural fatty oils. The resultant products are valuable plasticizers, stabilizers, diluents, and solvents for vinyl plastics and protective-coating formulations. The 90 to 100% concentrations represent a self-centered energy source which leaves no residue or corrosive gas, ideal for specialized propulsion units for aircraft, missiles, torpedos, and submarines. New uses are as a source of oxygen in municipal and industrial wastewater treatment systems and as an oxidant for in-place solution mining of low-grade uranium ores.

MANUFACTURE.[34] All hydrogen peroxide manufacturing plants built since 1957 utilize the autooxidation of an anthraquinone. The quinone is hydrogenated to the hydroquinone using either Raney nickel or palladium as a catalyst. Subsequent oxidation with air produces hydrogen peroxide and regenerates the quinone. The reactions can be illustrated with the easily oxidizable 2-ethylanthraquinone.



The hydrogen peroxide is water-extracted and concentrated, and the quinone is recycled for reconversion to the hydroquinone. A second organic process uses liquid isopropyl alcohol,

[34] *Du Pont Innovation* 5 (1) 5 (1973); ECT, 3d ed., vol. 13, 1981, p. 12.

which is oxidized at moderate temperatures and pressures to hydrogen peroxide and an acetone coproduct:

$$(CH_3)_2CHOH + O_2 \rightarrow (CH_3)_2CO + H_2O_2$$

After distillation of the acetone and unreacted alcohol, the residual hydrogen peroxide is concentrated.

An older electrolytic process produced hydrogen peroxide by the anodic oxidation of sulfate radicals to form peroxydisulfate intermediates.[35] Sulfuric acid electrolyte has low current efficiency (70 to 75 percent), but the use of ammonium sulfate causes crystallization problems, so a mixture is used to obtain a current efficiency of 80 percent or higher and yet not block the cell with crystal formation. The electrolyte is fed into a typical cell held at 35°C or below with platinum metal for the anode:

$$2H_2SO_4 \rightleftharpoons H_2S_2O_8 + H_2$$

The cell product, i.e., the persalt, or peracid, and sulfuric acid in water are subjected to hydrolyses at 60 to 100°C to yield hydrogen peroxide, as shown by the following simplified reactions:

$$H_2S_2O_8 + H_2O \rightleftharpoons H_2SO_4 + H_2SO_5$$
$$H_2SO_5 + H_2O \rightleftharpoons H_2SO_4 + H_2O_2$$

The electrolytic process requires that the electrolyte be continuously purified and also has very high capital and power requirements. Thus it cannot economically compete with the anthraquinone oxidation process.

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[35] *McGraw-Hill Encyclopedia of Science and Technology*, 5th ed., vol. 6, McGraw-Hill, New York, 1982, p. 747.

Chapter 6

Explosives, Propellants, and Toxic Chemical Agents

Many professional chemists and chemical engineers tend to view the subject of explosives and propellants from observation of their end-use effects, which are frequently spectacular and dramatic. Explosive manufacture is a constantly changing and growing field that greatly needs innovative professionals. The usual unit operations are applied here with new and frequently difficult constraints because of the nature of the products. Continuous processes are replacing batch ones for nitration, emulsification, and gelation with improved uniformity of product and lower cost. Recent advances in computer-controlled processing have found many applications in manufacturing. Commercial explosives are essential to such industries as mining and quarrying, construction, geophysical exploration, and metal cutting and forming. Major engineering jobs such as the construction of tunnels and dams would be impossibly expensive without explosives. Table 22.1 summarizes U.S. consumption of explosives.

HISTORY AND ECONOMICS. An explosive mixture of sulfur, charcoal, and saltpeter, called black powder, was known to the Chinese centuries ago; its use in propelling missiles was demonstrated shortly after 1300. The discoveries of nitroglycerine and nitrocellulose shortly before 1850, and the invention of dynamites and the mercury fulminate blasting cap soon after, were epochal events of the high-explosives era. Smokeless powder was first made in 1867. The demand for more powerful and uniform propellants for the space program offered a recent, new challenge. In times of war, increased quantities are required; for example, roughly 3×10^9 kg was manufactured in the United States between January 1940 and V-J day. Industrial and commercial use is very substantial: 1.6×10^9 kg/year in 1982. Although a great many compounds and mixtures are explosive, comparatively few of them are suitable for explosive use because of the critical restrictions on stability, safety, and price. Most explosive compounds are too expensive and too sensitive for much use.

TYPES OF EXPLOSIVES

An explosive is a material that, under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of a great deal of heat and much gas. The hot gases cause extremely high pressure if the explosive is set off in a confined space. Explo-

Table 6.1 U.S. Industrial Consumption of Explosives (in thousands of metric tons)

	1977	1978	1979	1980
Coal mining	952	986	1017	1138
Metal mining	203	261	279	254
Quarrying and nonmetal mining	238	275	297	284
Construction work and other uses	294	264	267	267
Total industrial	1687	1786	1860	1943

SOURCE: *Minerals Yearbook*, U.S. Bureau of Mines, 1982.

sives differ widely in their sensitivity and power. Only those of a comparatively insensitive nature, capable of being controlled and having a high energy content are of importance industrially or militarily. There are three fundamental types of explosives: mechanical, atomic, and chemical. This chapter is about chemical explosives. For purposes of classification it is convenient to place chemical explosives in two divisions in accordance with their behavior.

1. Detonating, or high, explosives. (a) Primary, or initiating, explosives (detonators); (b) booster and secondary explosives.
2. Deflagrating, or low, explosives.

There exists a very great difference between the detonating and deflagrating explosive types. High explosives detonate at very high rates, from 2 to 9 $\times$ 10^3 m/s, and the reaction front is a shock phenomenon moving actively throughout the material. Low explosives, or propellants, burn in layers parallel to the surface at low rates, around 10^{-2} m/s, and the reaction front is a flame.

Cook[1] lists the major explosive chemicals according to military or commercial use. Variations in their blasting characteristics are obtained by (1) altering physical conditions such as density and granulation and (2) combining ingredients—paraffin, aluminum, and waxes, for example. A table of nonexplosive additives appears in the same reference.

INITIATING, OR PRIMARY, EXPLOSIVES. Initiating, or primary, explosives are materials that are quite shock and heat sensitive and that can be made to explode by the application of a spark, flame, friction, or heat source of appropriate magnitude. They are very dangerous to handle and are used in comparatively small quantities to start the explosion of larger quantities of less sensitive explosives. Initiating explosives are generally used in primers, detonators, and percussion caps. They are usually inorganic salts, whereas booster and other high explosives and many conventional propellants are largely organic materials.

Primary explosives used include mercury fulminate [$Hg(ONC)_2$], lead azide $Pb(N_3)_2$, basic lead styphnate (trinitroresorcinate), diazodinitrophenol, and tetrazine (a complex conjugated nitrogen compound). Most priming compositions consist of mixtures of primary explosives, fuels, and oxidants. An example is 15% antimony sulfide, 20% lead azide, 40% basic lead styphnate, 20% barium nitrate, and 5% tetrazine. Glue, which acts as a binder, and ground glass, which increases internal friction, may be added.

[1]Cook, *Science of High Explosives*, ACS Monograph 139, Reinhold, New York, 1958, p. 4.; also Riegel, *Industrial Chemistry*, 7th ed., Reinhold, New York, 1974, pp. 676–683, this contains an extensive list, together with characteristics and uses.

BOOSTER HIGH EXPLOSIVES. Booster high explosives are materials that are insensitive to both mechanical shock and flame but that explode with great violence when set off by an explosive shock, such as that obtained by detonating a small amount of a primary explosive in contact with the high explosive. They are thus energy amplifiers. Decomposition proceeds by means of detonation, which is rapid chemical rupturing of bonds progressing directly through the mass of the explosive. Detonation is thought to be a chain reaction and proceeds at rates of around 6000 m/s. It is this high rate of energy release, rather than the total energy given off, that makes a product an explosive. Nitroglycerine has only one-eighth the energy of an equivalent weight of gasoline. On the other hand, most explosives, when unconfined and unshocked, will merely burn if ignited.

Important boosters are RDX (cyclotrimethylenetrinitramine), PETN (pentaerythritol-tetranitrate), and Tetryl (2,4,6-trinitrophenyl methyl nitramine). There are also some heat-resistant boosters, e.g., HMX (cyclotetramethylenetetranitramine).

BLASTING AGENTS. Blasting agents are powerful explosive agents that meet the criterion that they cannot be detonated by means of a No. 8 blasting cap when unconfined. They are, therefore, very safe to handle. A powerful booster is needed to start detonation.

SLURRY EXPLOSIVES. Slurry explosives are ammonium nitrate mixtures which frequently contain another oxidizer as well as a fuel dispersed in a fluid medium which, among other functions, controls the rheology of the gel-slurry.

EXPLOSIVE CHARACTERISTICS

Some very interesting technology has been used to determine the characteristics of explosives. Much is empirical, but measurements of heat values, rates of combustion and detonation, shattering ability, sensitivity, etc., reflect modern instrumental application to high-speed phenomena, and the results are a tribute to the skill and technology of explosives scientists and technicians.

Tests for sensitivity to impact and heat, stability on storage, shattering ability (brisance), explosive strength per unit weight, volatility, solubility, density, hygroscopicity, compatibility with other explosives, additives and possible metals used for enclosures, resistance to hydrolysis, and toxicity must all be run in a standard manner and taken into consideration.

The brisance of an explosive is measured by exploding a measured quantity of it in a sand bomb, a heavy walled vessel filled with a standard coarse sand which is crushed by the explosion. Screening measures the sand crushed, and from this the explosive force. Another test of a somewhat similar nature is the Trauzl block test. This test measures the strength of the explosive by measuring the ballooning of a soft lead cylinder in which the explosive is inserted and exploded. Results are reported in terms of the increase in volume, expressed in cubic centimeters, caused by the detonation of the explosive. Brisance is probably a combination of strength and velocity. Cook states that there is no reason to believe that brisance is power; it seems to be directly related to detonation pressure.[2]

The sensitivity of an explosive to impact[3] is determined by finding the height from which a standard weight must be allowed to fall in order to detonate the explosive.

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[2]Cook, op. cit., p. 271.

[3]Macek, Sensitivity of Explosives, *Chem. Rev.* 62, 41 (1962) (140 references).

It is important that explosives for use in mines, particularly coal mines, be of such a type that on explosion they evolve less than the specified amount of allowable toxic gases, as determined or specified by federal or state regulating agencies, and produce a minimum of flame. This latter requirement assures that the explosive is incapable of igniting mixtures of air and coal dust, or air and methane (the so-called fire damp), which inevitably occur in coal mines. Explosives for mine use are tested and their properties specified by the Bureau of Mines; they are commonly known as permissibles. Permissibles differ from other explosives, particularly black powder, most markedly in the fact that they produce a flame of small size and extremely short duration. Permissibles contain coolants to regulate the temperature of their flame, further reducing the possibility of igniting several types of combustible mixtures. Table 22.2 shows the characteristics of explosives.

INDUSTRIAL EXPLOSIVES

Cost per unit of work done (shattering of material or displacement without shattering) is almost as important as safety for industrial explosives. Present agents are less expensive and far safer than their predecessors.

HISTORICAL. Black powder has been the preferred blasting agent because it is less shattering in its effects. It is an intimate mixture of KNO_3, sulfur, and charcoal in the approximate proportions of 75:15:10. About 50 percent of the products of combustion are solids, giving its flames great igniting power, which is undesirable where combustible gases or solids are present but useful for igniting propellants.

Starting in 1860, dynamite dominated the blasting industry for a century, but its current use is small and diminishing.

BLASTING AGENTS AND SLURRY EXPLOSIVES. Blasting agents and slurry explosives have become the principal industrial explosives because they may be handled by simple machinery almost completely without danger and because their cost is very low. These are usually ammonium nitrate mixtures sensitized with nonexplosive fuels such as oil or wax. Properly initiated, such mixtures produce energies surpassing that of dynamite and are far cheaper. Ammonium nitrate is the world's most widely used explosive substance.

Cook lists the types and compositions of present-day industrial explosives (see also Table 6.3). Explosives play such a vital part in the nation's economy that their consumption has been suggested as a reliable index of the general scientific and technical atmosphere. See Table 6.4 for U.S. consumption of explosives in the mineral industry. The current energy crisis may well stimulate the use of explosives, particularly in mining coal and low-grade domestic ores.

NITROGLYCERIN AND DYNAMITE. Nitroglycerin was the first high explosive to be employed on a large scale. Nitration is effected by slowly adding glycerol of high purity (99.9% +) to a mixture having the approximate composition: H_2SO_4, 59.5%, HNO_3, 40%, and H_2O, 0.5%. Nitration is accomplished in 60 to 90 min in agitated nitrators equipped with steel cooling coils carrying brine[4] at 5°C to maintain the temperature below 10°C. After nitration, the

[4]Brine can be a little cooler than 5°C, but pure nitroglycerin freezes at 12.8°C. Freezing would be hazardous, since it might interfere with the temperature control.

Table 6.2 Summary of Characteristics of Explosives

Name	Formula	Products per Formula Weight	Q_v, J/kg	T_e, °C	f, kg/cm^2	V, m/s	Trauzl Expansion, cc/10 g	Potential, $\times 10^5$ kg-m
Gunpowder	$2KNO_3 + 3C + S$	$N_2 + 3CO_2 + K_2S$	2098	2090	2,970	—	30	2.1
Nitrocellulose	$C_{24}H_{29}O_9(NO_3)_{11}$	$20.5CO + 3.5CO_2 + 14.5H_2O + 5.5N_2$	5234	2800	10,000	6100	420	5.3
Nitroglycerin	$C_3H_5(NO_3)_3$	$3CO_2 + 2.5H_2O + 1.5N_2 + 0.25O_2$	6389	3360	9,835	8500	590	6.5
Ammonium nitrate	NH_4NO_3	$2H_2O + N_2 + 0.5O_2$	1608	1100	5,100	4100	300	1.6
TNT	$C_7H_5(NO_2)_3$	$6CO + C + 2.5H_2 + 1.5N_2$	2747	2200	8,386	6800	260	2.8
Picric acid	$C_6H_2(OH)(NO_2)_3$	$6CO + H_2O + 0.5H_2 + 1.5N_2$	3546	2717	9,960	7000	300	3.6
Ammonium picrate	$C_6H_2(NO_2)_3ONH_4$	$6CO + H_2O + 2H_2 + 2N_2$	2604	1979	8,537	6500	230	2.6
Tetryl	$C_7H_5N_5O_8$	$7CO + H_2O + 1.5H_2 + 2.5N_2$	3802	2781	10,830	7229	320	3.9
Mercury fulminate	$Hg(ONC)_2$	$Hg + 2CO + N_2$	1759	4105	5,212	3920	213	1.8
Lead azide	PbN_6	$Pb + 3N_2$	2864	3180	8,070	5000	250	2.9

SOURCE: After Meyer, *Science of Explosives*, Crowell, New York, 1943; for more recent investigations of characteristics of explosives, cf., Cook, *Science of High Explosives*, ACS Monograph 139, Reinhold, New York, 1958, p. 284, table 12.1; a more extensive list will be found in Riegel, *Industrial Chemistry*, 7th ed., Reinhold, New York, 1974, pp. 570–596.

NOTE: Q_v = heat of explosion at constant volume (small in comparison with fuels, but explosives exert their energy rapidly); T_e = explosion temperature, f = specific pressure, i.e., exerted by 1 kg in a volume of 1 L at T_e heat; V = velocity of detonation wave (currently measured by high-speed photography).

***Table* 6.3** Classes of Well-Characterized Slurry Explosives and Slurry Blasting Agents

Designation*	% Sensitizer	Oxidizer†	Water, % Nominal	Water, % Range
SE-TNT	17–60 TNT	AN, SN, BN, SC, NaP, C	15	8–40
SE-CB	15–35 CB	AN, SN, C	15	12–16
SE-SP	20–60 SP	AN, SN, BN, SC, NaP, C	15	2–20‡
SE-HSSP	20–60 HSSP	AN, SN, C	15	2–20‡
SE-TNT/Al	5–25/0.5–40 TNT/Al	AN, SN, NaP, C	15	10–30
SE-SP/Al	10–25/1–40 SP/Al	AN, SN, C	15	12–30
SBA-Al	0.1–40 Al 0–12 fuel	AN, AN/SN, AN/NaP, NaP	15	6–30‡
SBA-fuel	4.0–15 solid fuel	AN, AN/SN, NaP, SC	15	3–16‡

*TNT, trinitrotoluene, CB, composition B; SP, smokeless powder; HSSP, high-strength smokeless powder; fuel, various types—sulfur, gilsonite, other solid hydrocarbons, NH_4-lignosulfonate, others.

†AN, ammonium nitrate; SN, sodium nitrate; BN, barium nitrate; NaP, sodium perchlorate; SC, sodium chlorate; C, combinations (AN/SC incompatible).

‡Low percent requires water extenders, such as formamide, ethylene glycol, sugar, molasses.

SOURCE: *Ind. Eng. Chem* 60(7) 44 (1968). Reprinted with permission of the American Chemical Society.

mixture of nitroglycerin and spent acid is allowed to flow through a trough (a trough is easier to clean completely than a pipe) into separating and settling tanks some distance from the nitrator. The nitroglycerin is carefully separated from the acid and sent to the wash tank, where it is washed twice with warm water and with a 2% sodium carbonate solution to ensure the complete removal of any remaining acid. Additional washes with warm water are continued until no trace of alkalinity remains. See Fig. 6.1, where the quantities of raw material are also listed. The product is really glyceryl trinitrate, and the reaction is an esterification.

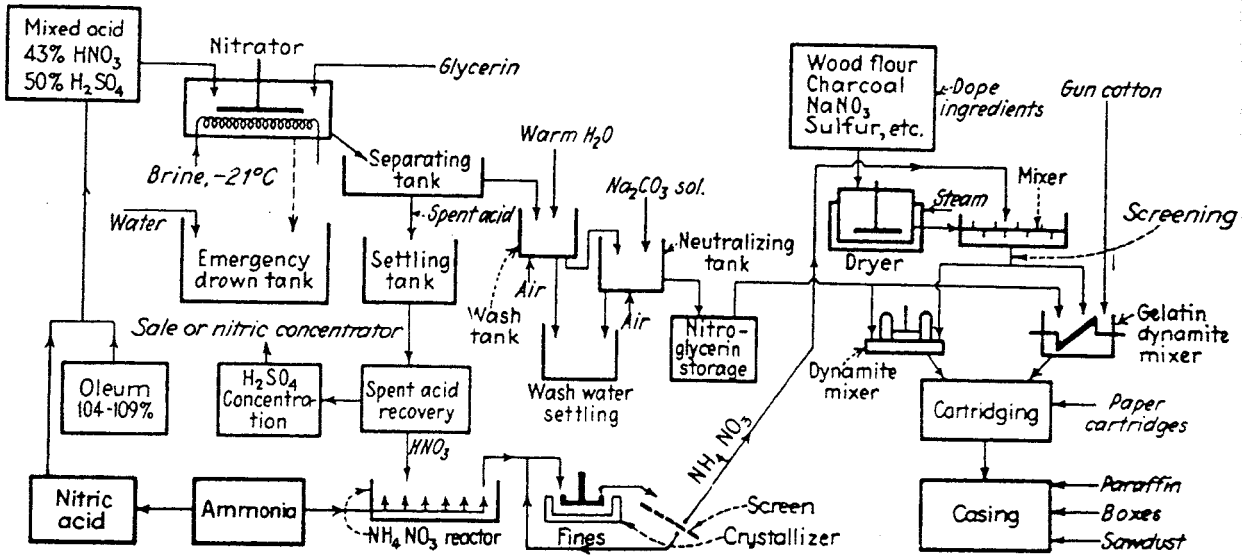
Small continuous stirred stainless-steel nitrators (Biazzi and other types) give higher yields, lower operating costs, and greater safety than the batch process illustrated in Fig. 6.1 because much less material is in process at any given time and control is easier. Most of the streams are in the form of emulsions, an inherently safer state. Other glycol nitrates are also made in continuous nitrators.

Nitroglycerin is a liquid similar in appearance to the original glycerol. It is sensitive to blows and freezes at 13°C; when solid it is less sensitive. The solid tends to explode incompletely, so frozen nitroglycerin must always be thawed before using. To make nitroglycerin

***Table* 6.4** U.S. Distribution of Consumption of Explosives in the Mineral Industry*
(Includes Coal Mining, Metal Mining, Quarrying, and Nonmineral Mining)

	1977	1978	1979	1980
Ammonium nitrate–fuel oil, mixed and unprocessed, %	85.5	83.9	83.8	85.9
Water gels and slurries, %	8.9	11.6	12.0	9.9
Other high explosives, %	4.0	3.4	2.9	2.7
Permissible explosives %	1.6	1.0	1.3	1.4
Total, thousands of metric tons	1392	1522	1587	1676

*Calculated from data in the *Minerals Yearbook, 1982*.



In order to produce 1 t of nitroglycerine, the following materials and utilities are required:

HNO_3 (100%)	1000 kg (10% recovered)	Refrigeration	1.5 t ice equivalent
H_2SO_4 (100%)	1000 kg (96% recovered)	Direct labor	5 work-h
Glycerin	430 kg		

Fig. 6 .1. Flowchart for the manufacture of nitroglycerin and dynamites. Usually an evaporator is needed between the ammonium nitrate reactor and the crystallizer.

safer and easier to handle, it is usually manufactured into dynamite. Dynamite was originally made by absorbing nitroglycerin into kieselguhr, a kind of clay. Modern dynamites generally use wood flour, ammonium nitrate, or sodium nitrate to absorb the nitroglycerin. Such a mixture is easy to handle and can be made to contain as much as 75% nitroglycerin and yet retain its solid form. Because of the demand for a nonfreezing dynamite for use in cold weather, dynamites containing other materials designed to lower the freezing point of the mixture are used, for example, glycol dinitrate. Such nonfreezing dynamites have potentials as great as "straight" dynamite. Nitrocellulose can be gelatinized by nitroglycerin, and the resultant firm gel is commonly known as gelatin dynamite. The ability to act as a combination plasticizer and explosive makes nitroglycerin and the similar diethylene glycol dinitrate (DEGN) useful in plastic explosives and smokeless powder manufacture. Almost without exception the nitro compounds and nitric acid esters used as explosives are toxic. The degree of toxicity varies widely with the material in question, but most are capable of causing acute distress if taken orally. Nitroglycerin has a small medical use as a vasodilator. Extremely toxic properties would weigh heavily against any new explosive that might be introduced.

PROPELLANTS, ROCKETS, AND MISSILES

PROPELLANTS FOR GUNS. The oldest propellant known is black powder, but its use today is trivial. It burns badly and far too fast for propellant use if the ingredients are left in finely divided form. Merely stirring the ingredients together produces useless material. Larger

grains are produced by intimate, intensive mixing, the mix actually being made into a dense colloid in a heavy-duty mixer. Black powder remains the best igniter available.

Smokeless powder replaced black powder for several reasons, its smokelessness, its superior power, and its better storage characteristics, but principally because it can be formed into stable grains whose size and shape governs the burning characteristics. This makes possible the construction of large rockets and guns. Smokeless powder is colloided cellulose nitrate, usually containing a plasticizer, such as nitroglycerin or nitroglycol. Sometimes a nonexplosive plasticizer such as dibutyl phthalate is added and usually about 1% of diphenylamine or similar amine designed to improve its storage life. When the only explosive used is nitrocellulose of over 13% nitrogen content, it is known as single-base powder; when two or more explosive ingredients are used (nitrocellulose and nitroglycerin), the grains are less brittle and the product is known as a double-base powder. Most sporting ammunition uses double-base powder. Military powders with grains over 25 mm in diameter are used in large rifles. Combustion of smokeless powder proceeds at a relatively constant rate in layers parallel to the ignited surface, so the speed of gas evolution (hence maximum bore pressure) is controlled by the geometry of the grain. Most rifle grains have internal perforations to control burning rates so as to be progressive bore pressure (increasing with time), neutral (constant with time), or degressive (decreasing with time).

NITROCELLULOSE.[5] The explosive properties of nitrated cotton were recognized at an early date. The discovery of methods for converting the material into a dense uniform colloidal mass reduced the surface and the rapidity of the explosion. With the discovery of suitable stabilization methods to prolong its storage life, nitrocellulose soon put black powder out of use as a propellant. Most nitrocellulose is now made from wood fibers rather than cotton.

The cellulose molecule is a complicated one, with a molecular weight frequently as high as 300,000. Any given sample of cellulose contains a wide distribution of molecules, all having the empirical formula $[C_6H_7O_2(OH)_3]_n$. There are thus three hydroxyl groups per fundamental (glucose) unit that may be esterified with nitric acid to yield a theoretical nitrogen content of 14%, which is higher than any commercially used product. The reaction is

$$C_6H\text{-}O_2(OH)_3 + 3HONO_2 + (H_2SO_4) \rightarrow C_6H\text{-}O_2(ONO_2)_3 + 3H_2O + (H_2SO_4)$$

Celluloses that have not been nitrated completely to the trinitrate are used as various industrial cellulose nitrates as shown in Fig. 6.2. In addition to nitrate esters, some sulfate esters are formed by sulfuric acid, which must be used to tie up the water resulting from the nitration reaction and to permit the reaction to progress to the right. These sulfate esters are unstable, and their decomposition would give rise to a dangerous acid condition in the stored powder if not removed; they are decomposed in the poaching process.

The finished nitrocellulose should not be allowed to become acid in use or in storage, since this catalyzes its further decomposition. A stabilizer is therefore added which reacts with any trace of nitrous, nitric, or sulfuric acid that may be released because of the decomposition of the nitrocellulose and thus stop further decomposition. Diphenylamine is used for smokeless powder (diphenylurea in Great Britain), and for celluloid, urea. The diphenylamine forms a series of innocuous compounds with the evolved gases.

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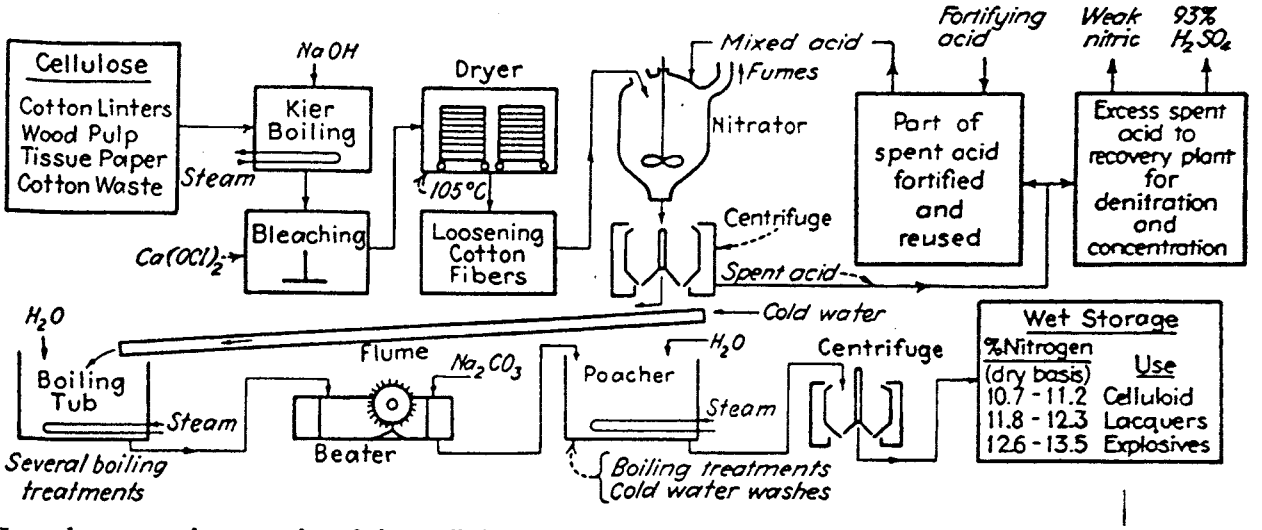
[5]Although the word "nitrocellulose" is commonly used for nitrated cellulose fiber, the material is not a nitro compound but a true ester of nitric acid. The name cellulose nitrate is therefore chemically more proper, but nitrocellulose is more widely employed in the industry.



In order to produce 2.2 kg of dry cellulose nitrate (0.75 kg raw cotton furnishes about 0.6 kg of purified cotton fibers), the following materials and utilities are required:

Cotton linters	0.75 kg	Chlorine	Variable but small
HNO_3 (100%)	1.0 kg	Water	227 L
H_2SO_4 (100%)	0.5 kg	Direct labor	0.03 work-h
Na_2CO_3	0.002 kg		

Fig. 6 .2. Flowchart for cellulose nitrate (nitrocellulose) manufacture. NOTE: Nitrogen content of cellulose nitrate is controlled by the composition of nitration mixed acid. Quality product depends on the grade of cellulose used and the care devoted to manufacturing procedures. Steps shown are for the military product. In use, wet product is dried by alcohol displacement.

The commercial manufacture of cellulose nitrate is illustrated in Fig. 6 .2 with the following steps:

Cotton linters, or wood pulp high in α-cellulose, are purified by boiling in Kiers (vats) with dilute caustic soda solution.

Bleaching is effected with CaClOCl, NaOCl, or $Ca(OCl)_2$.

The cotton is dried, fluffed, and weighed.

Mixed acid is made up from fortifying acid and spent acid, brought to proper temperature and run into the nitrator.

Nitration (esterification) is usually conducted under carefully controlled conditions in a "mechanical dipper" nitrator.

One nitrator charge is formed by 14.5 kg of purified cellulose. The cellulose is agitated with approximately 682 kg of mixed acid at 30°C for about 25 min. The composition of the acid used averages: HNO_3, 21%; H_2SO_4, 63%; N_2O_4, 0.5%; H_2O, 15.5%.

The entire nitrator charge is dropped into a centrifuge, where the spent acid is centrifuged from the nitrated cellulose.

The spent acid is partly fortified for reuse and partly sold or otherwise disposed of, e.g., by denitration and concentration of the H_2SO_4.

The nitrated cellulose is drowned with water, washed by boiling, and again washed in a beater.

In order to produce a smokeless powder that is more stable on storage, the following purification is employed to destroy unstable sulfate esters and to remove free acid completely. (This is a military procedure; commercially, the nitrated cellulose is dissolved in a solvent and neutralized chemically; this procedure works well and gives a stable product.)

Forty hours of boiling with at least four changes of water is followed by pulping of the fiber by means of a beater.

Poaching of the washed nitrated cotton by boiling first with a dilute Na_2CO_3 solution (2.5 kg of soda ash per metric ton of cellulose nitrate) and then many washes of boiling water.

The poached nitrocellulose is freed of most of its water by centrifugation. The water content is now approximately 28%.

At this point the nitrocellulose is usually stored and a laboratory examination made.

The water content of the nitrated cotton is reduced to a low figure by alcohol displacement of the water.

The nitrated cellulose is broken up and made into a dense colloid by mixing with alcohol, ether, diphenylamine, and other modifying agents.

Grains are formed by extrusion through dies, and these are dried and blended to form smokeless powder grains. The commonest shape is a pierced cylinder (macaroni) for small arms and a multiply pierced cylinder or rosette for larger guns.

The cellulose produced in this manner contains about 12.6% nitrogen and is known as pyrocotton. By using a stronger acid, the nitrogen content may be made as high as 13.6%. Cotton nitrated to contain 13.2% nitrogen or greater is known as guncotton. Modern military smokeless powder contains about 13.15% nitrogen and is made from a blend of pyro- and guncotton.

Smokeless powder is dense colloidal nitrocellulose containing about 1% diphenylamine and a small amount of a plasticizer such as dibutyl phthalate. The manufacture is shown in Fig. 6.3.

An interesting variant on this manufacturing process produces spheres, known as ball powder. The nitrocellulose, along with the additives, is dissolved in a solvent, e.g., mixed ketones, to form a lacquer which is then carefully emulsified with water. The emulsion is then inverted

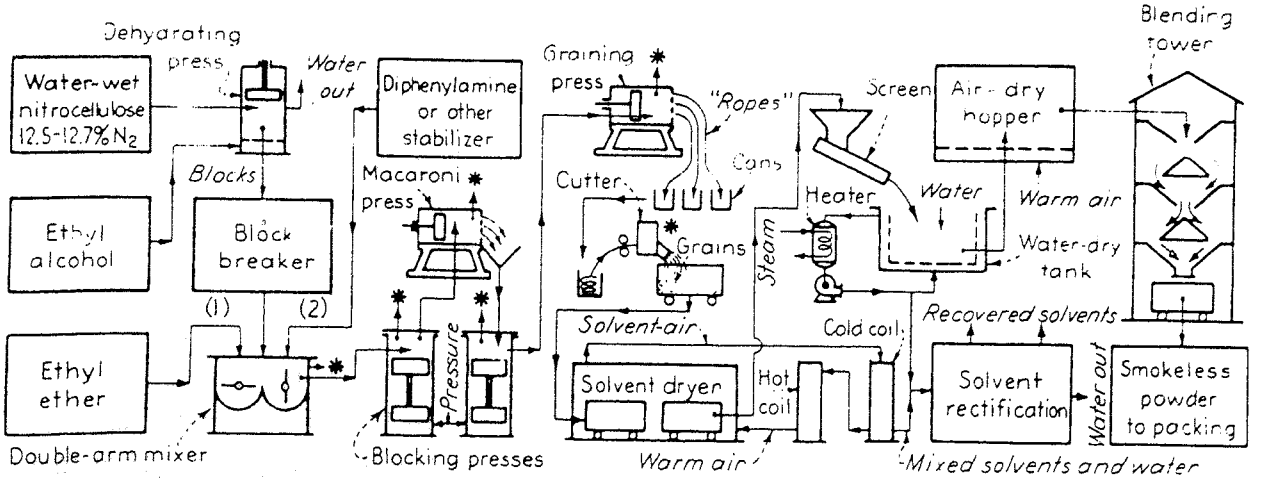


Fig. 6.3. Flowchart for single-base smokeless powder manufacture. For a flow sheet for nitrocellulose manufacture, see Fig. 6.2. NOTE: Asterisks denote equipment connected to solvent recovery system.

to give small spheres, and the solvent is driven off with heat. These spheres are sieved to give uniform size and can have nitroglycerine added to them to give double-base plasticized balls. Treatment with burning-rate regulators, such as dinitrotoluene, can cause the rate of burning to increase as the surface area for burning decreases. A sphere is the most degressive-burning shape possible. Proper treatment results in a progressive burning ball. Balls much above 3 mm are not practical, so only ammunition up to 50 caliber (0.5 in = 12.7 mm bullet diameter) is made. Much sporting ammunition is ball powder.

PROPELLANTS FOR ROCKETS

There are a great variety of choices in the design of efficient propulsion systems; liquids, solids, and castable solid units are all in use. Rocket propulsion systems derive their energy from chemical sources.

Rocket propellants[6] are low explosives which consist of fuels which include their own oxidant or other reactant necessary to cause the planned reaction. The thrust of the escaping hot gases pushes the device forward, according to the principle that forces act equally in opposite directions. High-performance systems under fine control are used for the launching of missiles and spacecraft for exploratory and scientific missions and for military offense and defense. Careful selection of the propellant ingredients is important to give high chamber temperature and pressure. The gases produced should be of low molecular weight. The reaction temperature may be so high that resistant structural materials are not available, in which case the temperature must be reduced. The fuel should be one which provides the greatest amount of heat for the smallest amount of weight. The foregoing factors are the most important ones in the equation defining *specific impulse*, or pounds of thrust per pound of weight of propellant burned per second, wherein the square root of the absolute temperature T divided by the square root of the average molecular weight M of the exhaust gases determines the value of the specific impulse: S. I. $= \sqrt{T}/\sqrt{M}$. Figure 6.4 shows the characteristics of major rocket propellants.

LIQUID PROPELLANTS.[7] Liquid propellants are those added to the combustion chamber as liquids. This includes all liquids used in a single propellant system, serving as fuel, oxidizer, and catalyst. Liquid fuels are, for the most part, used in bipropellant systems (fuel and oxidizer stored in two fuel tanks and fed separately to the combustion chamber). Monopropellants combine the fuel and oxidizer in one mixture. A few of the better-known liquid propellants are listed in Table 6.5, together with some of their characteristics. Liquid propulsion systems are the means for achieving the propulsive energy required for human space travel.

Large high-performance rockets now use LOX (liquid oxygen) and LH_2 (liquid hydrogen) propellants, because of their high specific impulse and low cost. Greater storage efficiency is achieved by catalytic conversion of nearly all the hydrogen to the para form. Large solid units are used where long storage time is required.

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[6]Tschinkel, Propellants for Rockets, *Chem. Eng. News* 32 (26) 2582 (1954) (excellent article with equations and tables); ECT, 3d ed. vol. 9, 1980, p. 620; Penner, Combustion and Propulsion Research, *Chem. Eng. News* 41 (2) 74 (1963).

[7]Kit, *Rocket Propellant Handbook*, Macmillan, New York, 1960.

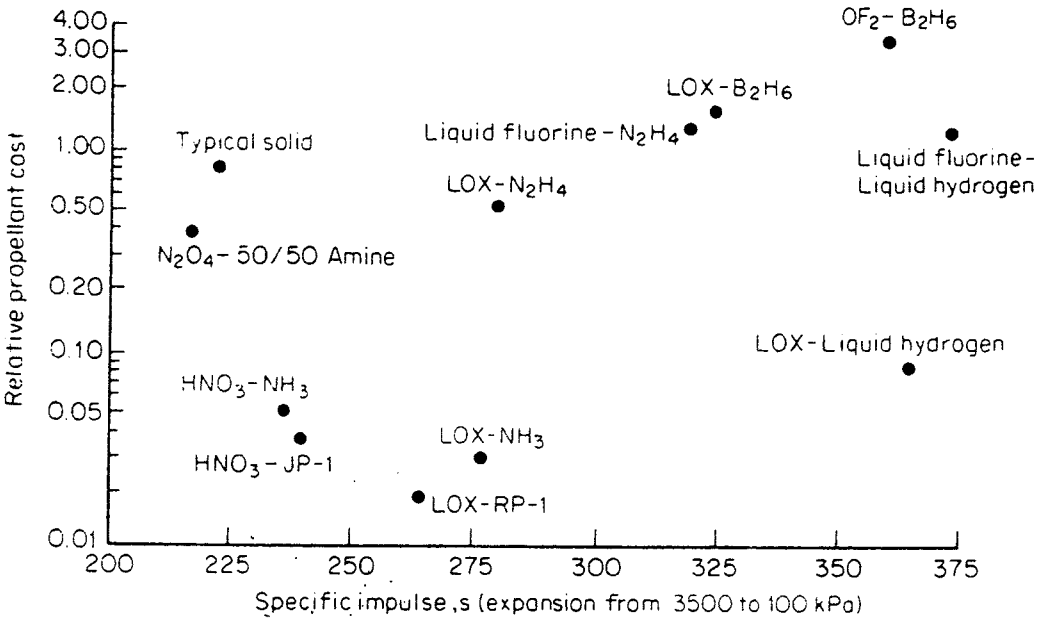


Fig. 6.4. Relative cost and specific impulse of rocket propellants. Note that the better the performance of the propellant, the higher the cost. LOX, liquid oxygen; N_2H_4, hydrazine; B_2H_6, boroethane (diborane); OF_2, oxygen difluoride; RP-1, kerosene hydrocarbon fuel; JP-1, jet fuel. [*Chem. Eng. News.* **41** *(39) 70 (1963) (modified 1975, 1982).*]

SOLID PROPELLANTS.[8] Solid propellants have advantages over liquids in that they are simple in design and more easily stored, handled, and serviced. They cost less and, because the ingredients are combined in a mold which serves to confine the materials and impart the desired grain configuration, they can be launched expeditiously, and predicted burning rates can be achieved. Originally, solids were classified into two groups: *heterogeneous, or composite* propellants (oxidizer and reducer present in two distinct phases) and, homogeneous, or double based (oxidizer and reducer present in a single or colloidal phase, e.g., nitrocellulose dissolved in nitroglycerin). Small percentages of additives are used to control the physical and chemical properties of the solid propellant. The properties of solid propellants are shown in Table 6.6.

Solid propellants have a variety of applications: as propulsion units for missiles, target drones, and supersonic sleds. Rockets used for the separation of stages during flight and for settling ullage in the liquid-propellant tanks are usually of the solid type; for example, some details of the Minute Man ICBM solid-propellant rocket stages are available.[9] Glass-filament wound casing for both the first and second stages of the submarine-launched Polaris carry a powerful solid propellant. The retro-rockets the Mercury capsule used for atmospheric reentry employed solids. Flowcharts and equipment have not been released, but processing methods have been described.

Artificial satellites are another type of spacecraft that require rocket propulsion for launch-

[8]Sutton, *Rocket Propulsion Elements*, 3d ed., Wiley, New York, 1963; Kit, op. cit.; Solid Groundwork for Solid Rockets, *Fortune* **71**, 114(March 1965)(excellent illustrations of case and nozzle fabrication for "modern and fierce compounds that strain the polymer chemist's newfound art").

[9]*McGraw-Hill Encyclopedia of Science and Technology*, vol. 11, McGraw-Hill, New York 1982, p. 723.

***Table* 6.5** Current Propellants

Propellant	Application	Specific Impulse*	Density	Combustion Temperature, °C
O_2/C_2H_5OH (92.5%)	Redstone	287	0.99	3116
O_2/RP-1	Atlas, Thor, Jupiter, Titan I, Saturn, F-1 engine	301	1.02	3400
O_2/H_2	Centaur, Saturn, J-2 engine, M-1 engine	391	0.28	2730
WFNA†/JP-4	Small aircraft engines	268	1.33	2960
IRFNA‡/UDMH	Agena, Able	277	1.25	2955
IRFNA/60% JP-4 + 40% $(CH_3)_2N_2H_2$	Bomarc A	269	1.31	2930
N_2O_4/50% N_2H_4 + 50% $(CH_3)_2N_2H_2$	Titan II, Titan III, Trans, Apollo	288	1.21	3090
$N_2O_4/(CH_3)N_2H_3$	Gemini	288	1.21	3116
IRFNA/MAF§	Bullpup B	270	1.31	2760
90% H_2O_2/JP-4	Small aircraft engines	266	1.29	2525
90% H_2O_2 monopropellant	Mercury, many others	151	1.39	760
N_2H_4 monopropellant	Mariner, Ranger	191	1.01	621

*Pounds of thrust per pound of weight of propellant burned per second. See text.

†WFNA, White fuming nitric acid.

‡IRFNA, Inhibited red fuming nitric acid.

§MAF, Mixed amine fuel.

SOURCE: *Chem. Eng. Prog.* 60 (7) 73 (1964).

***Table* 6.6** Solid Propellants for Rockets

Propellant Type	Castable Composite	Extruded Double-Base*
Propellant system	Oxidizer-fuel, $NH_3ClO_4,(C_2H_4O)_n$	NC, NG, miscellaneous
Typical ingredient variation, %	$KClO_4$ (50–85), $(C_2H_4O)_n$ (50–15)	NC (50–60), NG (30–45), miscellaneous (1–10)
Adiabatic flame temperature, C°	1540–2480	2100–2900
Typical sea-level specific impulse	175–240	205–230
Characteristic velocity, km/s	1.16–1.46	1.37–1.52
Density, g/cm^3	1.52–1.74	avg. 1.61
Lower combustion limit, kPa	>1360	
Probable allowable operating-temperature limits, C°	−57 to 112	−29 to 96
Storage stability	Good	Fair
Smoke	Much at low oxidizer; little at high oxidizer, mist at relative humidity greater than 80%.	Little
Mechanical properties	Soft and resilient to hard and tough	Hard and tough

ing. Several have been placed in the earth's orbit, some for communications (Telstar), for meteorological observations (Zeros), for scientific measurement, for human space flight, and to detect nuclear explosions

MISCELLANEOUS INDUSTRIAL EXPLOSIVE USES

There are a number of industrial procedures which make use of small quantities of explosives which are highly important. Explosive rivets can be placed without backing devices. Explosive thrustors, pin pullers, separators, and release devices were extremely reliable on the space missions and find use in industrial emergency devices. Forming, shaping, and cladding metals by explosive welding have become important manufacturing techniques. Explosive welding is used to form plate heat exchangers. Shearing and punching of metals works very well. Ejection seats are explosive powered. Electrical cable and connectors are now being attached by firing explosive charges. Metal powders are compacted into formed shapes by use of explosives. Wherever a directed, reliable, swift blow can accomplish a task, an explosive may well be the preferred choice. Much remains to be discovered.

PYROTECHNICS

Because of antifireworks laws, the pyrotechnics industry has now only a fraction of its former importance. Pyrotechnic mixtures, however, still have a number of uses: illuminating flares, marine signal rockets, the red signal flare (fusee) used by trucks and trains for signaling an emergency, and colored light mixtures used for military purposes. In general, these products consist of mixtures of strong oxidizing agents, easily oxidizable materials, and various other materials which act as binders and which alter the character of the flame, together with the color-producing chemical itself. A typical composition used in the manufacture of illuminating flares contains the following materials: barium nitrate (oxidizing agent), 34%; magnesium (to give heat), 36%; aluminum powder (to give strong light), 8%; sodium oxalate (to give a yellow tint), 20%; and calcium stearate, castor oil, and linseed oil (as binders), 2%. As this formula does not fire readily, an igniter consisting of a mixture of 75% black powder and 25% of the above formula is always used to start the flame. A mechanical device starts the combustion of the formula.

MATCHES

The manufacture of matches is an essential industry that is highly mechanized. At present, practically all matches fall within two categories, safety matches and strike-anywhere matches. The match head composition of the latter consists essentially of a fuel with a low kindling point, usually phosphorus sesquisulfide (P_4S_3), an oxidizing agent such as potassium or barium chlorate, ground glass, and glue. Safety matches are ignited by the generation of heat on the striking surface of the box, the coating of which consists mainly of red phosphorus, ground glass, and glue. No phosphorus sesquisulfide is used in safety matches, but antimony sulfide is used in the heads as a flame-producing agent.

MILITARY EXPLOSIVES

Cost is less vital in the case of military explosives and the accent is on performance and good storage life. More organic materials are used than in industrial work, but ammonium nitrate remains the major explosive substance.

A complete round of ammunition is everything necessary to fire a shot. Military ammunition varies in size from caliber 30 (0.30 in = 7.6 mm bullet diameter) to 17 in = 432 mm weapons. The essential ingredients for a complete round of high-explosive ammunition is shown in Fig. 6.5.

The unit consists of a thin cartridge case holding the primer, igniter, and propellant charge. The case is designed to fit smoothly into the gun and, on explosion, to expand, sealing the breech of the gun so that the escape of gases to the rear is prevented, thus allowing the full effect of the propellant to be exerted on the projectile half of the shell. The primer contains a small amount of a priming mixture [e.g., $KClO_3$ + $Pb(CNS)_2$ + Sb_2S_3 + TNT + ground glass]. This mixture explodes under the impact of the firing pin and produces a flame which ignites the black powder charge of the igniter which in turn ignites the propellant charge of coarse-grained smokeless powder. The burning of the smokeless powder causes the rapid emission of heated gas, which ejects the projectile from the gun. At the target, upon impact or upon functioning of the time-fuze mechanism, a small quantity of a primary explosive (the detonator) is set off; this causes explosion of the booster—an explosive of intermediate sensitivity (between that of a primary explosive and the bursting charge)—which picks up the explosive shock from the detonator, amplifies it, and ensures complete detonation of the bursting charge. The bursting charge of high explosive is usually TNT alone or mixed with ammonium nitrate. Most bursting charges are mixtures, for example amatol (TNT + NH_4NO_3), compound B (RDX + TNT), pentolite (PETN + TNT), tetratol (tetryl + TNT), and octol (aluminum + TNT + NH_4NO_3). Ammonium picrate is used for armor-piercing shells because of its extraordinary resistance to shock. Industrial and military explosives both use the same chain initiator–primer (blasting cap), booster (booster), bursting charge (blasting agent) pattern, except for the fuze, which is some type of mechanical or electronic device to cause explosion on impact, delayed on impact, or by proximity, as desired.

Many military explosives have at least some industrial use, which is not surprising, since many military and industrial uses are similar. Smokeless powder, black powder, and primers have all been discussed earlier. Military units tend to be larger, the performance demanded requires better quality control, and the effects of really long-time storage under difficult conditions must be minimized. Some major explosives used are listed below.

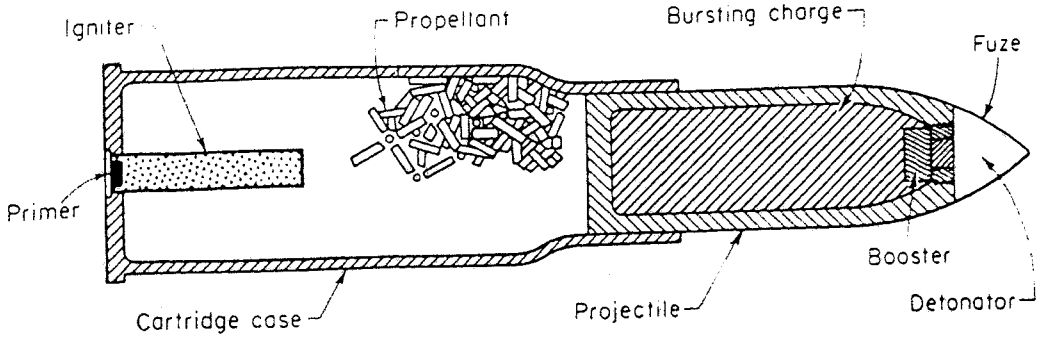


Fig. 6.5. Complete round of high-explosive ammunition.

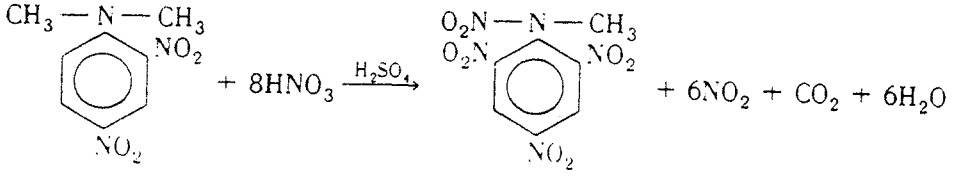
TNT (Trinitrotoluene)

In spite of other new explosives developed, symmetrical TNT remains an important military explosive, particularly in mixtures with ammonium nitrate. Its low melting point (80°C) permits loading into bombs and shells in the molten state. It does not have picric acid's tendency to form shock-sensitive metallic salts. TNT is made by multiple-stage nitration of toluene with a mixture of nitric and sulfuric acids. Three-stage nitration to mono-, di-, and trinitrotoluene was formerly used, but continuous-flow stirred-tank reactors and tubular units using the countercurrent flow of strong acids and toluene permit better yields, control, and lower costs.[10]

Tetryl

Tetryl [2,4,6-trinitrophenylmethylnitramine, $C_6H_2(NO_2)_3NCH_3NO_2$] is chiefly used as a base charge in blasting caps, as the booster explosive in high-explosive shells, and as an ingredient of binary explosives. It is generally prepared by the action of mixed sulfuric and nitric acid on dimethylaniline in a multiple-stage nitration.

$$C_6H_5N(CH_3)_2 + 2HNO_3 \xrightarrow{H_2SO_4} C_6H_3N(CH_3)_2 \cdot NO_2 \cdot NO_2 + 2H_2O$$



$$+ 8HNO_3 \xrightarrow{H_2SO_4}$$

$$+ 6NO_2 + CO_2 + 6H_2O$$

It may also be made by alkylating 2,4-dinitrochlorobenzene with methylamine and then nitrating.[11] Tetryl is a powerful high explosive with intermediate sensitivity and great shattering power.

Picric Acid

Picric acid (2,4,6-trinitrophenol) is not made by the direct nitration of phenol, because too many oxidative by-products are formed. It is manufactured instead by the nitration of mixed phenolsulfonates with mixed acid.[12] Mixed acids cut down the health hazard caused by fuming, reduce the amount of acid required, and increase the yield of desired products. The use of mixed acid is now almost universal. Its heavy-metal salts are dangerously sensitive, and its major use is for the manufacture of ammonium picrate.

Explosive D

Explosive D, or ammonium picrate, is made by the neutralization of a hot aqueous solution of picric acid with aqueous ammonia.

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[10]Albright, Processes for Nitration of Aromatic Hydrocarbons, *Chem. Eng.* 73 (10) 161 (1966); Prime, Seven-Stage Nitration of TNT, *Chem. Eng.* 71 (6) 126 (1964).

[11]*Military Explosives*, Depts. of the Army and Air Force, Technical Manual TM9-1910, April 1955, p. 157.

[12]Formerly, strong nitric acid alone was used.

It is used in armor-piercing shells as a bursting charge. Because is a salt, it does not melt so it must be loaded by compression.

PETN

PETN, pentaerythritol tetranitrate $C(CH_2ONO_2)_4$, is one of the most brisant and sensitive of the military high explosives. For use as a booster explosive, a bursting charge, or a plastic demolition charge, it is desensitized by admixture with TNT or by the addition of wax. PETN may be made by the nitration of pentaerythritol with strong (96%) nitric acid at about 50°C. The reaction of decomposition is probably:

$$C(CH_2ONO_2)_4 \rightarrow 3CO_2 + 2CO + 4H_2O + 2N_2$$

PETN is used in making detonating fuses and commercial blasting caps, and has a small medicinal use.

RDX

RDX, cyclonite, or *sym*-trimethylenetrinitramine $[(CH_2)_3N_3(NO_2)_3]$, is one of the most powerful explosives known at the present time. RDX is used in a mixture with TNT and aluminum, known as Torpex, for mines, depth charges, and torpedo warheads. It is also employed as an ingredient in explosives for shells and bombs and is desensitized by wax or oily materials. Pentolite, made by casting slurries of PETN with TNT, has specialized uses; for example, 50:50 pentolite is used as a booster for slurry blasting agents and prilled ammonium nitrate–fuel oil mixtures and as the main charge in Procore boosters. The British developed the first practical synthetic process, which involved the destructive nitration of hexamethylenetetramine with concentrated nitric acid:

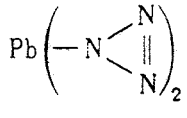
$$C_6H_{12}N_4 + 3HNO_3 \rightarrow C_3H_6O_6N_6 + 3HCHO + NH_3$$

A combination process was developed by Bachman at the University of Michigan, who utilized the by-products to obtain a second mole of RDX. This method was developed on a continuous scale by Tennessee Eastman, which manufactured it the most economically (yields of 70 percent).

$$C_6H_{12}N_4 + 4HNO_3 + NH_4NO_3 + 6(CH_3CO)_2O \rightarrow 2C_3H_6O_6N_6 + 12CH_3COOH$$

Some by-products of this reaction are also useful as explosives.

Lead Azide



Lead azide has largely replaced mercury fulminate as an initiating explosive for blasting caps. The fulminate has less than desirable stability, has to be manufactured in small batches, and

involves scarce and poisonous mercury. Lead azide has remarkable stability, involves no strategic materials, and can be manufactured in large batches by treating sodium azide with lead acetate or nitrate. Sodium azide can be made from sodium amide and nitrous oxide.

$$NaNH_2 + N_2O \rightarrow NaN_3 + H_2O$$
$$2NaN_3 + Pb(C_2H_3O_2)_2 \rightarrow Pb(N_3)_2 + 2Na(C_2H_3O_2)$$

Lead Styphnate

Styphnic acid is trinitroresorcinol and forms two salts on reaction with lead acetate or nitrate, basic lead styphnate [$C_6H_2(NO_2)_3OPbOH$], and lead styphnate. The basic styphnate is a favored primer ingredient. Styphnic acid can be prepared from dinitrochlorobenzene, but nitration of resorcinol gives very poor yields.

INCENDIARIES

Flammable mixtures are probably the oldest chemical weapons known to humans; the destruction of many ancient cities was due to the use of fire. Samson tied firebrands to the tails of foxes and ran them through the Philistine's grain fields. Incendiaries were the largest single category of chemical supplies consumed during World War II and were vital factors in that victory. An incendiary, strictly speaking, causes ignition of combustible materials at the target, e.g., wooden buildings or petroleum products. Incendiaries take the form of bombs, bomblets, artillery shells, and grenades. Incendiaries fall into two classes, metallic and petroleum. Metallic incendiaries provide intense sources of ignition, petroleum units scatter less intense sources widely. Metallic incendiaries include bombs with metallic cases, usually made of a combustible magnesium alloy filled with a mixture of barium nitrate and aluminum with thermite to ignite the case. Thermite is a mixture of aluminum powder and iron oxide which, when ignited, burns fiercely at a high temperature and cannot be extinguished by means of water.

$$3Fe_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Fe \qquad \Delta H = -3.01 \text{ MJ}$$

Some readily ignitable material, such as black powder, is employed to ignite the thermite. Sometimes white phosphorus or a small amount of tetryl is added as a deterrent to fire fighters.

Petroleum incendiaries contain gasoline thickened with various ingredients. The first satisfactory thickener was rubber, but other thickeners such as isobutyl methacrylate polymer, which was dissolved in gasoline in combination with calcium soap, were discovered. Perhaps the most important thickener is napalm. This is a granular aluminum soap prepared by precipitating aluminum sulfate in excess alkali with two parts of acids from coconut oil, one part of naphthenic acid, and one part of oleic acid. The soap is capable of withstanding elevated temperatures and produces a gasoline jelly at ordinary temperatures by simple mixing. Napalm surpasses rubber gels in effectiveness and is applicable in flame throwers where rubber gels would be too viscous. It was because of napalm that the flame thrower became such an important and formidable weapon.

Flame weapons provide the fuel for a fire which destroys the target by heat, e.g., personnel, weapons, or electronic equipment. Flame weapons are usually massive bombs or armored, vehicular-mounted flame throwers. Flame weapons also ignite combustible material present at the target. Flame throwers enjoy a limited use for controlling unwanted vegetation.

TOXIC CHEMICAL WEAPONS

Modern use of toxic chemicals in war began in 1915, with the release of a large quantity of chlorine, a gas which was rather ineffective because of its low molecular weight and consequent high diffusion rate which made it difficult to create and maintain casualty-producing concentrations in the areas desired. Contact poisons such as "mustard gas" were more effective. Such agents are persistent because of low vapor pressure. A variety of improved toxic agents have been devised containing both chemical and biological materials. Used against an unprepared enemy, these agents are very effective. Used as a defensive weapon to deny an area to an enemy, these agents might be useful, but as an offensive weapon they require difficult decontamination before advancing troops can enter. Protective clothing and self-contained breathing apparatus hamper movement and greatly reduce effectiveness. Use of toxicants is universally condemned, but mutual fear and distrust keeps interest in their development alive.

Toxic agents designed to produce temporary incapacity are of value in controlling riots and civil disobedience. Such materials may produce sneezing, tears, vomiting, and/or nausea. Gas masks are rarely effective and self-contained breathing apparatus is required for adequate protection. Common tear gases include chloroacetophenone, brombenzylcyanide, and *o*-chlorobenzylmalonitrile.

SCREENING SMOKES

Smokes or persistent fogs are used to hide areas on a temporary basis. Smokes are dispersed by mechanical, thermal, and chemical means. Most fogs are created by forming low volatile droplets of water which remain dispersed in air. White phosphorus, which burns to P_2O_5; hexachloroethane-zinc combustion, which forms $ZnCl_2$; and sulfur trioxide, and chlorosulfonic acid, which gives off HCl and H_2SO_4, are used to create chemical nuclei for fog formation. Oil vapor mists are used in smoke grenades. Colored smokes are made by burning pyrotechnic mixtures which volatilize various heat-resistant organic dyes.

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Chapter 7

Photographic Products Industries

The word "photography" is derived from two Greek words which mean "drawing by light." Vision is the most common method humans have at their disposal for receiving and conveying impressions of the world in which they exist—ample proof of the importance of photography to modern civilization. There is no field of human activity at the present time, whether it be industry, science, recreation, news reporting, printing, or the mere recording of family histories, which is not, in some phase or other, touched upon by the photographic process. Although it is one of the youngest of the chemical process industries, it has universal appeal.

HISTORICAL.[1] The first recorded use of a lens for image formation occurred in the latter part of the sixteenth century. The effect of light on silver salts was known to the early alchemists, but it was Wedgwood, son of an English potter, who at the beginning of the nineteenth century first successfully reproduced images as negatives on paper impregnated with silver salts. In 1819, Herschel discovered the fixing properties of *sodium thiosulfate*, thus paving the way for permanent pictorial reproductions and making possible the first exhibit, in 1839, of so-called "photographs." The same year, a Frenchman, Daguerre, released to the public his formula for the manufacture of the familiar daguerreotype, and an American, Draper, made what was probably the first photographic portrait.

The announcement of these processes created a demand for better lenses, which was soon satisfied. In 1851, Archer improved and perfected the "wet-collodion" process, but in the hands of the public all the collodion processes eventually bowed to the superior gelatin dry plate discovered by Maddox. Vogel at the University of Berlin in 1873 discovered that dye molecules adsorbed on the silver halide crystals greatly increased the light sensitivity of these crystals (spectral sensitization). In 1889, George Eastman introduced transparent roll film and popularized the now familiar snapshot camera. Soon after this, practical methods for producing motion pictures were invented. Color-sensitized emulsions were used as early as 1904 by the Hoechst Dye Works of Germany, and the famous Wratten panchromatic plates were introduced in 1906. Velox developing paper was announced in America at about the same time, as the result of the discoveries of Leo H. Baekeland. Portrait film was introduced about 1920, and projection printing came into general use about the same time. Since the early 1920s, developments in all phases of the art have been fundamental and rapid, culminating in the introduction of natural color film about 1928 and practical amateur color prints in 1941. It is this latter field, color photography, that now holds the most promise for the future. The present advanced position of the photographic industry was attained as a result of thorough research on the fundamentals in this field and their application.

[1]ECT, 3d ed., vol. 17, pp. 611–656, 1982.

USES AND ECONOMICS. Photography finds widespread application. The amateur uses it in three major ways, for prints (both "instant" and from color negatives), home movies, and small transparencies. Professional usage is more varied: entertainment, education, sales promotion, graphic reproduction in magazines, display advertising, industrial illustration, data recording, nondestructive testing including photography, and medical and scientific records. In the United States 14 percent of the products are purchased for medical use, 13 percent by professional movie makers, 14 percent for photocopying and reproduction, 25 percent by business and commercial users, and 36 percent by amateurs. It is estimated that yearly more than 6×10^9 still pictures—about 85 percent in color—are made by amateurs. In home movies, color film has almost completely (99 percent) displaced black-and-white.

PHOTOGRAPHIC PROCESS

Photography is the process of producing a visible image upon a substance by the action of light or other radiant energy. Thus ultraviolet and infrared are included as initiators, and the word "light" encompasses that portion of the electromagnetic spectrum from the ultraviolet region through the visible region and into the infrared. In the case of the economically significant photographic processes, the "light" sensitive substances employed are silver halides, diazo compounds, amorphous selenium, organic photoconductors, and zinc oxide. Silverless films are widely used for medical x-rays, graphic arts, and engineering drawings. They have not taken over the consumer market because they are *slow* compared with silver halide film.

A new development that threatens to take over some of the silver film market is the introduction of an electronic camera which uses videotape instead of film to produce the image.

Silver halides are employed as the sensitive substance in the most widely used photographic materials.[2] Such materials have a natural sensitivity to ultraviolet and blue radiation. Their sensitivity to green, red, and infrared is negligible unless special sensitization to these regions is induced by adsorption of so-called sensitizing dyes on their surfaces. Sensitization to blue, green, and red is particularly important in the representation of colors as shades of gray in black-and-white photography and in their simulation in color photography. Light-sensitive silver salts are prepared in the dark as aqueous gelatin "emulsions" which, after proper additional treatments, are coated on a support which may be glass, paper, plastic, or some other material. Although manufacturers closely guard exact procedures employed in preparing commercial emulsions, the general principles are described in the literature.[3] The technology is complicated, and the user of photographic materials generally purchases a packaged coated product.

Exposure of the emulsion in a camera or other suitable device results in a photochemical reaction on the surface of the silver salt crystal. Photolytic silver, constituting a *latent image*, forms roughly in proportion to the amount of incident light of the color to which the crystal is sensitive. The latent image serves to catalyze further conversion of the entire crystal to a

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[2]The photographic industry used 1650 t (53×10^6 troy ounces) of silver in 1981; *Chem. Week* **130** (26) 13 (1982).

[3]Sturge, (ed.), *Neblette's Handbook of Photography and Reprography*, 7th ed., Van Nostrand Reinhold, New York, 1977; Duffin, *Photographic Emulsion Chemistry*, Focal, London, 1966.

metallic silver image upon the action of a developing agent. The density of the image depends upon the number of crystals exposed and the extent to which development is permitted to occur. Crystals which did not become exposed or were insensitive to the exposing light develop slowly or not at all. Removal of these silver salts and the undeveloped portions of those which had been exposed is accomplished by the formation of soluble complexes, which are later washed from the material by water. The result of this process is an image whose density bears a direct relationship to the intensity of the initiating light energy. Thus a light object is reproduced as a dark image, and vice versa. When the sensitive material is exposed in a camera, the result of the process described above is a negative. Positives, or prints, are generally produced by using the negative to modulate the exposure of a second piece of photographic material, followed by processing as above.

Recent technological advances have brought direct-positive or reversal camera films to the market. Direct-positive photographic images are obtained by first developing the negative silver image and then dissolving the silver in an oxidizing solution or "bleach." The residual complement of silver halide, which has the configuration of the positive image, is uniformly fogged either physically by light or chemically by a reducing agent and then developed to give a positive silver image.

PHOTOGRAPHIC EQUIPMENT AND MATERIALS. All *films* and *plates* consist essentially of an emulsion on a film support of cellulose acetate, polyester, or glass. The *emulsion* is composed of a suspension of minute silver halide crystals in gelatin, suitably sensitized by the addition of certain dyes or various classes of sulfur and gold compounds. In addition, antifogging agents, hardening agents, stabilizers, coating aids, and an antihalation backing are used. Halation is fogging of the emulsion by light reflected into it from the back surface of the film. The back of the film is generally coated with a layer of hardened gelatin to prevent curling. Table 7.1 lists important photoprocessing chemicals and their functions.

PROCESSING OF BLACK-AND-WHITE MATERIALS. Modern developing solutions contain mainly four functional constituents: an organic reducing agent, a preservative, an accelerator, and a restrainer. The function of the *reducing agent* is to chemically reduce the silver halide to metallic silver at the various points where light has produced the latent image. As this reduction is a rate process, practical *developers* are those which reduce silver halide in contact with a latent image to silver much faster than they reduce the silver halide unaffected by light. Chemically, they are polyhydroxide, amino hydroxide, or polyamine derivatives, and are mostly aromatic. The developing agents which are commercially important are hydroquinone, *p*-methylaminophenol (Elon, Metol), certain heterocyclic substances such as Phenidone, and *p*-phenylenediamines. The last mentioned are particularly important in color photography and will be discussed further. *Preservatives* guard the developer against air oxidation. The most common is sodium sulfite, but the bisulfite and metabisulfite are also employed. *Accelerators* increase the alkalinity of the developing solution, hence increase the activity of most of the developing or reducing agents. They include the carbonates of sodium and potassium, sodium metaborate, and borax. Antipollution laws in several states have caused the use of borates and borax to be discontinued. In order to control the speed of the developer, it is necessary to employ a *restrainer,* usually potassium bromide or a heterocyclic compound such as benzotriazole.

The theory of the development of the photographic image is connected with the properties of the emulsion. In the silver halide crystals internal dislocations act as electron traps. When a minute amount of light energy is absorbed by the silver halide, a free atom of silver is

Table 7.1 Selected Photoprocessing Chemicals Used in Black-and-White Photographs
(Chemicals Represent Approximately 2% of Processing Costs)

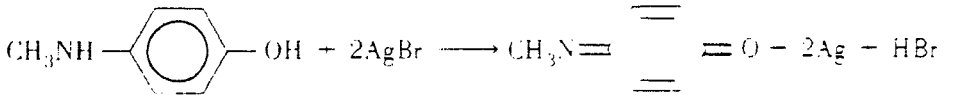
Use	Common or Trade Name	Chemical Name	Action
Developing agents			
Capable of reducing exposed crystals of silver halide in emulsion to silver without reducing unexposed crystals at the same time	Hydroquinone	*p*-Dihydroxybenzene	Slow, powerful
	Metol. Elon	*p*-Methylaminophenol	Fast
	Phenylenediamine	*p*-Phenylenediamine	True grain (toxic)
	Phenidone	1-Phenyl-3-pyrazolidone	Forms superadditive mixtures with other developing agents
Activators			
Activate developing agent and control pH		Sodium carbonate	Controls pH
		Potassium carbonate	Controls pH
Preservatives			
Guard against oxidation		Sodium sulfite	Transforms oxidation products into colorless compounds
Prevent staining of emulsion		Sodium carbonate	
		Sodium citrate	
Restrainers			
Prevent chemical fog		Potassium bromide	Lowers degree of ionization of silver bromide
		6-Nitrobenzimidazole	
		Benzotriazole	
Calcium precipitants			
Prevent sludging	Calgon	Sodium hexametaphosphate	Forms complex compounds
	Quadrafos	Sodium tetraphosphate	Forms complex compounds
Wetting agents			
Facilitate absorption of developing solution	Denatured alcohol	Ethyl alcohol	
Neutralizer		Acetic acid	Stops development by acidification
Fixatives			
Dissolve unexposed silver halides	Hypo	Ammonium thiosulfate	Converts silver halides into water-soluble compounds
		Sodium thiosulfate	
Hardeners			
	Aluminum, chromium, and ferric salts	Chrome alum	Hardens gelatin to insolubilize it and increase mechanical strength
	Organic aldehydes	Glyoxal, formaldehyde	
Intensifiers			
Increase density	Chromium compounds	Potassium dichromate	
	Silver compounds + hypo		

Table 7.1 *(continued)*

Use	Common or Trade Name	Chemical Name	Action
Reducers			
Reduce density	Potassium ferrocyanide with hypo		Varies with concentration; oxidation of silver
	Potassium permanganate and sulfuric acid		

SOURCE: Augmented from Glafkides, *Photographic Chemistry*, Fountain [illegible] 1958; modified from *SPSE Handbook of Photographic Science and Engineering*, Wiley, New York, 1973.

liberated. This silver atom acts as a center which attracts more photolytically generated silver atoms until a positively charged stable latent image site capable of being developed (Ag_2^+) is formed. This latent image is changed into a visible image by the developer's depositing sufficient metallic silver from the silver halides of the emulsion on these nuclei. In the presence of sufficient sulfite, a typical developer, *N*-methyl-*p*-aminophenol (Metol) probably reacts as follows:



Development is arrested at the desired point by immersing the photographic material in a mildly acid bath, usually dilute acetic acid, which destroys the alkaline condition necessary for development.

Modern *fixing agents* are of a nonhardening or acid-hardening type. Their main purpose is to render the silver image permanent by dissolving away the undeveloped silver halide. The type most commonly employed includes a silver halide solvent (sodium or ammonium thiosulfate), an antistaining agent (acetic or citric acid), a preservative (sodium sulfite), and a hardening agent (potassium chrome alum or formaldehyde).

The processing of black-and-white photographic materials is concluded by a *wash* in running water to remove the silver halides solubilized by the fixing baths. Thorough washing is necessary for long-term stability of the image to avoid staining and bleaching due to decomposition of unremoved silver complexes. After washing, the materials are dried, often with heat. Where long-term stability or highest quality is not necessary, or where rapid access to the final image is desired, stabilization processing is sometimes employed. This process often consists of two baths: a conventional developer, followed by the stabilizing bath itself, which often contains sodium thiosulfate, potassium thiocyanate, or urea. The silver complexes thus formed are not washed from the material.

The photographic process may be summarized by these steps: exposure of the negative film or plate in a camera, followed by development of the latent image, fixing of the image by removal of the unaffected but still sensitive silver halides, and drying of the negative. The negative is used to make a positive, usually on paper, which is subjected to the same sequences of exposure, development, fixation, and drying.

The recovery of silver from used processing solutions is important both from economic considerations and because of environmental concerns. Silver is also recovered from discarded negatives and prints and scrap film.

Several methods for silver recovery are described in great detail in the patent literature. The common methods are electrolytic plating out of the silver from the spent solutions using a stainless-steel cathode or by the immersion of two dissimilar metals in the solution. The silver in solution can also be precipitated as free silver from solution by reduction with steel wool, zinc dust, or hydrosulfites and by treatment with sulfides to precipitate silver sulfide.

Reverse osmosis is one of the more recent methods of removing silver salts from solution. The silver halides can be extracted with an acidified water-nitrile mixed solvent, and the solvent solution subjected to reverse osmosis through a suitable membrane to concentrate the silver salts.

COLOR PHOTOGRAPHY—THEORIES, MATERIALS, AND PROCESSES

Color photography[4] is based upon the principle that the colors of nature can be adequately represented to the eye and brain by mixtures of blue, green, and red light. Such mixtures have been produced by projecting in register colored beams of light emanating from properly prepared transparent positive images or by modulating, by silver images, microscopic blue, green, and red filters which are juxtaposed on a support. In the latter method, the eye receives from any area of the picture the amounts of blue, green, and red necessary to reproduce the intended color in that area. A color television picture tube is an electronic analog of this system.

The use of blue, green, and red beams or filters is difficult in practice and is wasteful of light energy. Most methods of color photography are based on the *complements* of blue, green, and red, which are yellow, magenta, and cyan, respectively. Yellow results when blue is absent from white light; magenta, when green is absent; and cyan, when red is absent. Thus a yellow filter controls the blue component of white light while permitting green and red to pass; magenta controls green while permitting blue and red to pass; and cyan controls red while permitting blue and green to pass. Therefore combinations of various densities of yellow and magenta produce a variety of colors, including orange and red; yellow and cyan produce greens; and magenta and cyan produce blues. These combinations can be effected by superimposed dye-containing layers on a single support.

Originally color prints were prepared by applying layer upon layer of pigment to a single print. This process has become almost obsolete with the advent of the much more convenient dye-transfer system. However, there is still some interest in the pigment process because prints thus produced have much more permanent colors than those produced with dyes.[5]

The upper cross section in Fig. 7.1 shows the arrangement of blue-, green-, and red-sensitive emulsion layers and the effect of exposure. A yellow filter layer prevents blue light from reaching the green- and red-sensitive layers, which retain sensitivity to blue. The dyes are located as shown in the other sketches, depending on the color-product objective. Dyes with properties suitable for color photography are produced when the development is accomplished by *p*-phenylenediamines in the presence of an active species called a *coupler*. The

[4]Thirtle, Inside Color Photography, *CHEMTECH* 9 (1) 25 (1979); ECT, 3d ed., vol. 6, 1979, pp. 617–682.

[5]*Wall Street Journal*, July 1 1981, p. 48.

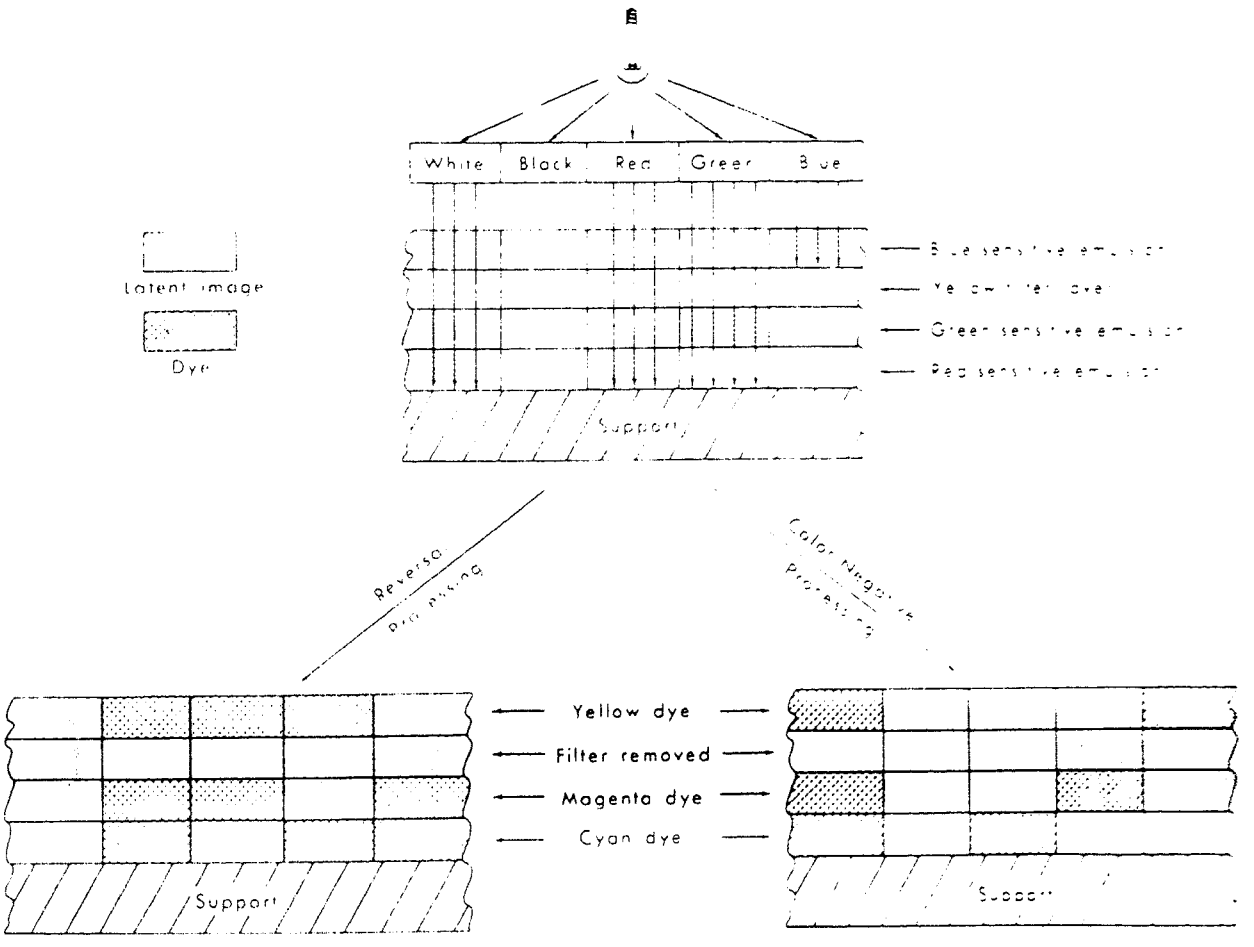
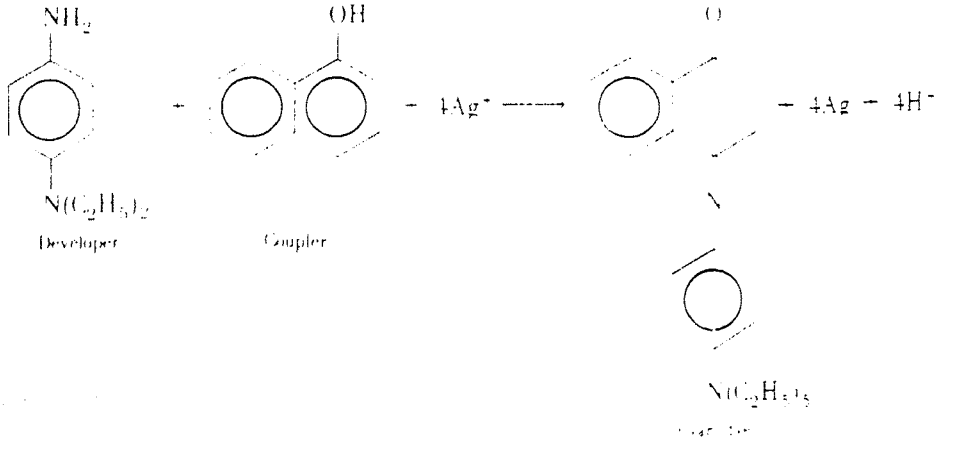


Fig. 7.1. Relation of dye images to the selective sensitivity of color photographic emulsions. (*Courtesy Kodak Co.*)

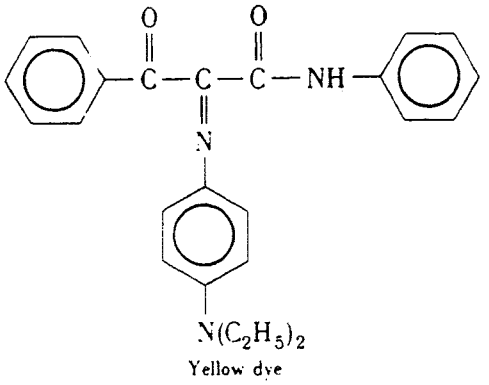
dye-forming reactions are:

$$\text{Exposed silver salt} + \text{developer} \rightarrow \text{oxidized developer} + \text{silver}$$
$$\text{Oxidized developer} + \text{coupler} \rightarrow \text{dye}$$

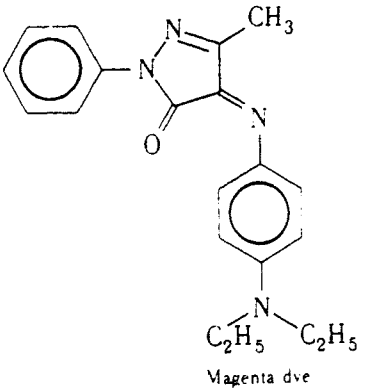
In the case of the specific developer, *N*,*N*-diethyl-*p*-phenylenediamine, and a specific coupler, α-naphthol, the overall reaction can be written



This dye, of the indoaniline class, is cyan. From benzoylacetanilide as the coupler, a yellow dye of the azomethine type results, and from a pyrazolone, a magenta dye is formed:



Yellow dye



Magenta dye

Such dyes are of the Kodachrome type and involve inclusion of the coupler in the developer solution. *Such a process requires that only one layer develop at a time and that all reactants be washed out of the photographic material before the next dye is produced.* Careful control is needed to prepare each layer for development. If, however, the bulk of the coupler is increased so that it cannot diffuse through gelatin and certain other characteristics are introduced, the coupler can be incorporated in the emulsion by the manufacturer. The exposed silver salts can then be developed in all layers simultaneously. The oxidized developer finds the proper coupler in the immediate vicinity and therefore forms the proper dye in the amount required by the subject.

There are two major types of color photographic processing, negative and reversal, as indicated in Fig. 7.1. *Negative processing* involves incorporated couplers and results in color development in the region of the exposed silver salts. A color negative results in dyes complementary to the colors of the subject. Thus a yellow dye is formed in regions exposed to blue, a magenta dye in regions exposed to green, and a cyan dye in regions exposed to red. This negative can be used to make a positive print or any number of intermediate color pictures in order to introduce special effects, as in color cinematography. In making the print, the dyes in the negative control the amounts of blue, green, and red light reaching the color-sensitive emulsion layers on the print material. The latter emulsions, like those of the negative, contain incorporated couplers.

Reversal processes involve the development of exposed silver salts to a silver negative. The remaining silver salts are exposed selectively, and color developed to yield dye layer by layer, as in Kodak Kodachrome film, or are exposed or chemically fogged in toto and developed to yield dyes in all layers simultaneously, as in Kodak Ektachrome film, which contains incorporated couplers

New processes of color photography are being introduced. One of these, *Polacolor* (Fig. 7.2), a product of the Polaroid Corp., depends upon incorporation in the light-sensitive layer of preformed dyes to which developing agents are chemically attached. The process is accomplished as described above by sensitized emulsion layers. The dye developers are soluble in the alkaline processing solution; however, as an image is developed, the dye developer is converted to an insoluble, immobile form. Dye-developer molecules not involved with image development diffuse from the emulsions and are mordanted on a receiver, which becomes the print.

Polaroid's SX-70 system[6] involves the exposure of the film and its almost immediate exit

[6]Fast Film, Powerful Battery Improves Polaroids, *Chem. Eng. News* 59 (25) 52 (1981); Land, One-Step Photography, *Photog. Sci. Eng.* 16 (4) 147 (1972).

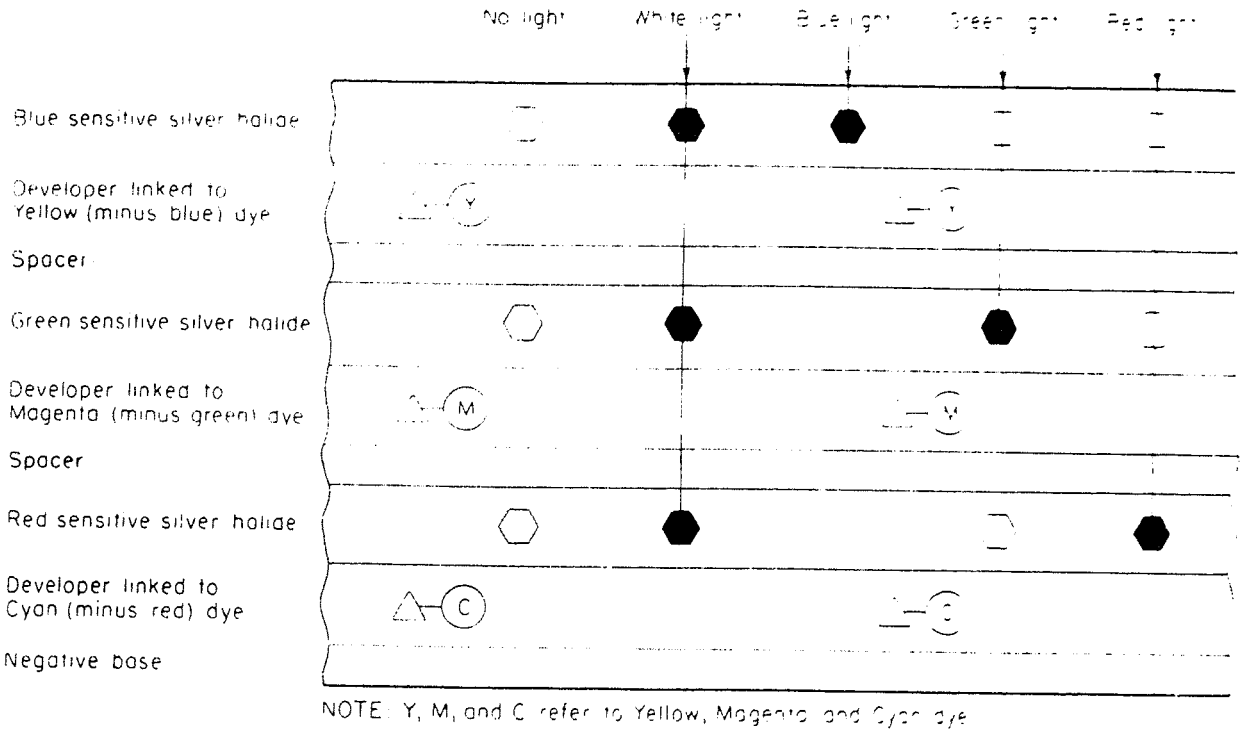
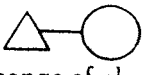


Fig. 7.2. Development process of Polaroid-Land cameras. Structure of the negative. The principal layers of the negative are shown *magnified 6000 times*. The total thickness of all these layers coated on a sturdy base) is less than half the thickness of a human hair.



This symbol represents an entirely new kind of molecule, which is a dye linked to a developer by an inactive atomic thread. This nonconducting leash does not allow interchange of electronic charges between the dye and developer, but it does give the developer group control over the movement of the dye. The dye part of these hitched molecules must be different in each layer.

These are unexposed grains of silver halide.

These are exposed grains of silver halide. Note, for example, how a ray of green light will pass through the blue-sensitive layer without exposing the silver halide and will expose a grain in the green layer, but not in the red layer.

In Polaroid cameras, where the exposure and development processes are carried on in the camera itself, the inventor Land uses a novel method of development for both black-and-white and color pictures, wherein the processing liquid is spread from "pods" in a thin viscous layer between the negative and the positive as the two are pressed together. Land developed the diffusion-transfer-reversal (DTR) process. This process produces a finished positive black-and-white or colored picture in a remarkably short time and directly from the camera. The Polaroid color film contains an entirely new kind of molecule developed for this use, namely, a dye (yellow, magenta, or cyan) in different layers linked to a developer by an inactive thread. Upon development (pod broken), the reagent reaches all parts of the extremely thin layers and, as it reaches a linked molecule of developer and dyer, it sets the linked molecules in motion.

When a linked molecule reaches a light-exposed silver grain, it becomes involved in the development of that grain and loses its mobility and acts to form its part in the image on the positive; e.g., a ray of green light exposes a silver halide in that layer and traps a linked molecule of developer and magenta dye. Likewise, this happens for other colors of light, building up the complementary color. All these unite together in their respective layers to form the color positive. *(Polaroid Corp.)*

from the camera into many million times as much light as is used to expose it. This was accomplished by synthesizing indicator dyes that have high absorption coefficients at high pH values and that become colorless at lower pH values. The exposed film passes through the rollers of the camera which force a small quantity of alkali and titanium dioxide between the layers. The dissolved dye developers diffuse upward through the emulsion layers. When an exposed silver halide grain is met, the developers are oxidized and immobilized within the emulsion. Molecules of dye developers that do not come into contact with exposed grains

continue to move upward to the polymeric mordant layer where they form the positive color image. The titanium dioxide acts to prevent further exposure of the film outside the camera and also serves as the white background for the positive image. This system uses a positive working chemistry and a negative emulsion.

Kodak[7] has introduced an instant color process that uses a negative working chemistry and a reversal emulsion. In this system the dyes are attached to immobile carriers, not dye couplers. The activator fluid is highly alkaline and causes the release of the dye from the carrier. To produce a positive dye image specially developed silver halides are used with nucleating agents in each light-sensitive layer. The sensitivity centers in the silver halide crystals attract the photoelectrons when exposed to light. No latent image sites are formed on the surface of the exposed crystals and the unexposed crystals form surface-latent image sites because they have weak internal attractions for photoelectrons. The dyes are released at the point where the development occurs and thus do not migrate as in the Polaroid system.

MANUFACTURE OF FILMS, PLATES, AND PAPERS

In the making of photographic films, plates, and papers, three distinct steps are carried out: (1) preparation of the light-sensitive emulsion, (2) manufacture of the base or support for the emulsion, and (3) coating of the emulsion on the base. Figure 7.3 gives a general representation of the manufacturing steps involved.

EMULSIONS. The so-called photographic emulsion is in reality not a true emulsion but rather a suspension of finely divided silver halide grains in gelatin. The gelatin serves as a mechanical binder, a protective colloid, and a sensitizer for the halide grains.[8] The manufacture of the emulsion usually requires ripening and addition of chemicals to control speed, contrast, stability, fog, and sensitivity to desired wavelengths. Hardeners are also added to improve the thermal stability and mechanical durability of the gelatin. In the manufacture of emulsions for color photography, other additions such as dyes and dye couplers are made.

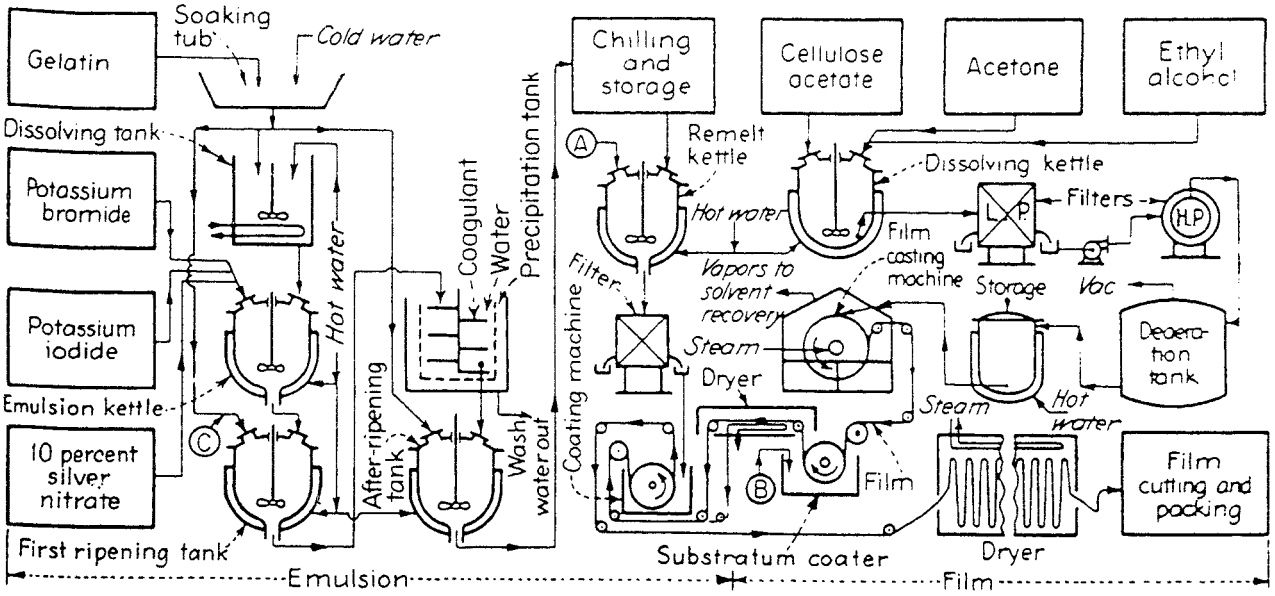
Silver halides are sensitive only to wavelengths shorter than 500 nm (the ultraviolet, violet, and blue wavelengths). When nonsensitized silver halides are used, the resulting ordinary emulsion reproduces blues as light and greens and reds as dark. Dyes can be added to increase the halide sensitivity (spectral sensitivity). If the sensitivity is increased to 600 nm (the green wavelengths), the resulting halide emulsion is known as *orthochromatic* and reproduces blues and greens as light and red as dark. When additional dye is added to sensitize the halide to 700 nm (red wavelengths), the *panchromatic* emulsion reproduces good tone values of all the colors.

Table 7.2 shows the types of chemicals used in preparing photographic emulsions. The halide used influences the speed of the emulsion: Ag_2Br_2 and small amounts of Ag_2I_2 produce fast emulsions, while for slower emulsions, Ag_2Cl_2, Ag_2Br_2, and Ag_2ClBr are used. The finished emulsion generally consists of 35 to 40% silver halide, 65 to 60% gelatin, and small amounts of the special-use chemicals.

The silver halide is precipitated in the presence of gelatin by treating silver nitrate with the appropriate potassium halide. The gelatin acts as a protective colloid and allows suspension of the microcrystalline silver halide. These microcrystals produce a very "slow" emulsion

[7]Kodak Details Chemistry of Instant Film, *Chem. Eng. News* 54 (26) 32 (1976).

[8]Duffin, op. cit.



In order to produce 1000 m^2 of film, the following materials (in kilograms) are required (the solvents are mostly recovered):

Potassium bromide	110	Cellulose acetate	220
Potassium iodide	0.29	Glycerin	245
Gelatin	39.2	Ethyl alcohol	297
Silver nitrate	9.8	Acetone	579

Fig. 7.3. Flowchart for the production of photographic film. Extreme cleanliness must be practiced and an appropriate safety light provided after the silver halide has been formed. NOTES: A, Chrome alum, preservative (phenol or thymol), saponin, KBr, and sensitizing dyes are added here. B, Gelatin and solvent used for substratum coating. C, Gelatin added at close of ripening period.

***Table* 7.2** Chemicals Used in Preparing Black-and-White Photographic Emulsions

Use	Chemical	Action
Mechanical, protective binder	Gelatin	Base in which to form halide dispersion
Image formation	Silver halides	Forms latent image site when exposed to light
Chemical sensitization	Thiosulfates and thiourea	Increases light sensitivity (speed)
Chemical sensitization	Stannous chloride and sodium sulfite	Reducing agents to increase sensitivity
Chemical sensitivity	Gold salts—as ammonium aurothiocyanate	Increases sensitivity
Stabilization	Triazoles, tetrazoles, or iminazoles	Stops chemical sensitization
Spectral sensitization	Cyanine dyes	Increases wavelength sensitivity
Hardeners	Aldehydes and chromium salts	Increases thermal stability and resistance to abrasion
Antifogging	Potassium bromide, benzimidazoles, benzotriazoles, and mercaptotetrazoles	Stabilizes chemical sensitization to prevent photographic fog
Uniform coating of emulsion on base	Surfactants	Controls surface tension of gelatin and acts as spreading agent

so a ripening process is necessary to allow larger grains to be formed. The small crystals, being more soluble than the large ones, tend to dissolve and reprecipitate on the large crystals. The finished crystal size ranges from 0.1 to 0.3 μm.[9]

The ripened emulsion is leached with cold water to remove any soluble salts and then heated with a compound that will form silver sulfide specks at the grain surface. The sensitivity of the silver halide can be increased from 10 to 100 times by this process. If one silver atom out of 10^5 atoms is converted to silver sulfide, it is sufficient. For very sensitive film a small amount of a gold salt is added.

After the emulsion has been chemically sensitized, dyes are added to spectrally sensitize it so that it will reproduce good tones from all the wavelengths of visible light. Before coating the emulsion on the support, it is customary to add chrome alum or formaldehyde as a hardening agent. Phenol or thymol may be introducd to prevent growth of mold or bacteria. The addition of KBr at this stage aids in the prevention of fog. The introduction of amyl alcohol or saponin serves to depress the surface tension of the liquid emulsion, facilitating uniform foam-free spreading on the support.

EMULSION COATING. The sensitized emulsion may be coated on glass, plastic, or paper depending upon the end use. Glass provides the most dimensionally stable support, but its weight and fragility make it unsuitable for any use but precision photography. Clear plastic supports are the most widely used in modern photography while paper is used for print materials.

Various methods of coating the support with the emulsion are in use. Usually the support is moved on rollers past the coating station. The liquid emulsion may be in a trough, and the support is brought in contact with the surface of the emulsion. Excess emulsion is removed by air jets or by a knife edge. Alternately, the emulsion may be spread over the support by pumps or gravity flow from hoppers. The coated support is cooled to gel the emulsion and then dried to remove most of the water. The finished layer is only about 10 percent of the original thickness.

The finished product consists of several separately applied emulsion layers. An intermediate layer is used to prevent stray light from reflecting back into the sensitized emulsion during exposure. A final coat of especially hardened gelatin is used for protection of the emulsion surface.

Color film requires many layers of emulsion, each one sensitive to one of the three colors (blue, green, and red). Some color films have more than six coatings. Each layer is applied separately and dried before the next one is applied, although the patent literature claims that up to six layers can be coextruded onto a ramp and then transferred to the film base without intermixing of the layers, which would be a catastrophe in the manufacture of color film.

SPECIAL APPLICATIONS OF PHOTOGRAPHY

PHOTOMECHANICAL REPRODUCTION FOR ILLUSTRATIONS.[10] Photography has found one of its most important applications in the reproduction of photographs on the printed page by means of printing inks. These processes may be classified as (1) *relief printing,* also referred

[9]*Focal Encyclopedia of Photography,* Focal, London, 1969.

[10]For brief technical descriptions of these processes, see CPI 2, p. 592.

; photoengraving, in which the raised portion of a plate receives the ink for transference ıe paper, and so-called *line* plates and *halftone* plates are used; (2) *intaglio* printing, :h includes photogravure, rotogravure, and metal engraving, in which the relief printing edure is reversed and the hollow regions of the plate or metal cylinder hold the ink; (3) *ographic* printing, or lithography,[11] which makes use of the inability of a water-wet sur- to take ink. The *offset printing process* utilizes lithographic plates which are particularly ıtable to illustrative work in color, and the usual separation negatives are used in their aration.

ıotopolymerization, or polymerization initiated by light, has the ability (as has silver le photography) to amplify the effect of light enormously; the multiple effect, however, rs simultaneously with exposure, rather than in a separate processing step. This method ıeen used extensively in the printing field. The Kodak Photo Resist process for making ɔengravings was introduced in 1954; it uses the cross-linking of a photopolymer system. il photopolymer printing plates, which use photosensitive acrylic plastic bonded to l, were marketed in 1960, and the time for making a plate has been reduced to ¼ h as ɔared with 4 h needed for making a conventional metal engraving. A photopolymer ing plate formed by the light-induced cross-linking of nylon has been described in the ture.[12] In 1964 a process called *panography* was introduced—the first successful use of to create a three-dimensional effect on a flat surface. A thin film of transparent plastic rial, called Epolene, is applied to produce the effect, and a special press is used for the ss.[13]

'OCOPYING.[14] Photographic copying of documents reaches back to the earliest days of ıgraphy. Although newer methods of photocopying have largely replaced the earlier in which visible images are produced on exposure of prepared paper, some of these *ing-out processes* are capable of producing exceptionally fine prints, and others afford tain control over tone values unequaled by any other process. Several have been bed by Neblette; among them are the silver, chromate, and iron processes. Herschel ɔped the *blueprint process* in 1842, a method dependent on the ability of ferric ions to luced to ferrous ions in the presence of organic matter under the influence of strong Paper is coated with ferric ammonium citrate and potassium ferricyanide. When a line ng is placed over the prepared paper and then exposed to light and treated with water, oluble blue image is formed where the light reaches the paper; this image is in prussian ferric ferrocyanide ($Fe_4[Fe(CN)_6]_3$). The cyanotype, or positive blueprint (where lines ue and background light), uses a more radiation-sensitive ferric mixture and, processed potassium ferricyanide solution, yields Turnbull's blue, ferrous ferricyanide $'e(CN)_6]_2$).

839—the same year that two other milestones in photography were reached—Breyer mented with silver halide–coated paper to copy pages from books. However, the first sful document-copying device not requiring especially prepared originals was the Rec- h, invented about 1900. Other projection photographic copying machines followed, ing the Photostat, but all had their shortcomings. Contact-box printers were introduced

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'iginally, lithography meant engraving on stone and printing therefrom, a process not urrently except for special work in small quantities.

ıem. Eng. News 42 (30) 91 (1964).

aphic Advance, *Barron's*, May 25, 1964, p. 3.

:T, 3d ed., vol. 20, 1982, p. 128, gives an excellent description of various processes.

in the 1930s, but they did not meet the demand for speed and easy operation. It was not until the *diffusion-transfer reversal process* was patented about 1940 that the revolution in copying methods began. These copying techniques are image-forming processes which create essentially full-sized copies of the original and should not be confused with office duplicating processes such as mimeographing, multilithing, or the newer adherography. Copiers reproduce directly from an original document, while duplicators reproduce through the use of an intermediate master.

The most widely used photocopying process is the *electrostatic process* invented by the Xerox company in 1937, but not commercially available until 1950. Figure 23.4 shows the essential details of this process. Because the electrically charged selenium is an integral part of the drum, plain paper can be used. The *Electrofax* process is similar to the *Xerox*, but it uses an electrically charged zinc oxide–coated paper instead of the selenium-coated drum.

Among other processes are (1) thermography, which uses the heat of infrared rays for exposure and requires that the original have carbon or a metallic compound in the text ink and thus cannot copy colored originals; (2) dry silver process (electrophotographic); (3) electrolytic process; and (4) wet transfer processes. Table 7.3 lists some of the most popular processes.

MICROFILMING. Microphotography is the art of making miniature photographic facsimiles of original materials. It is currently used by insurance companies, banks, and engineers for commercial records in active use or for security purposes. This method is also used by libraries

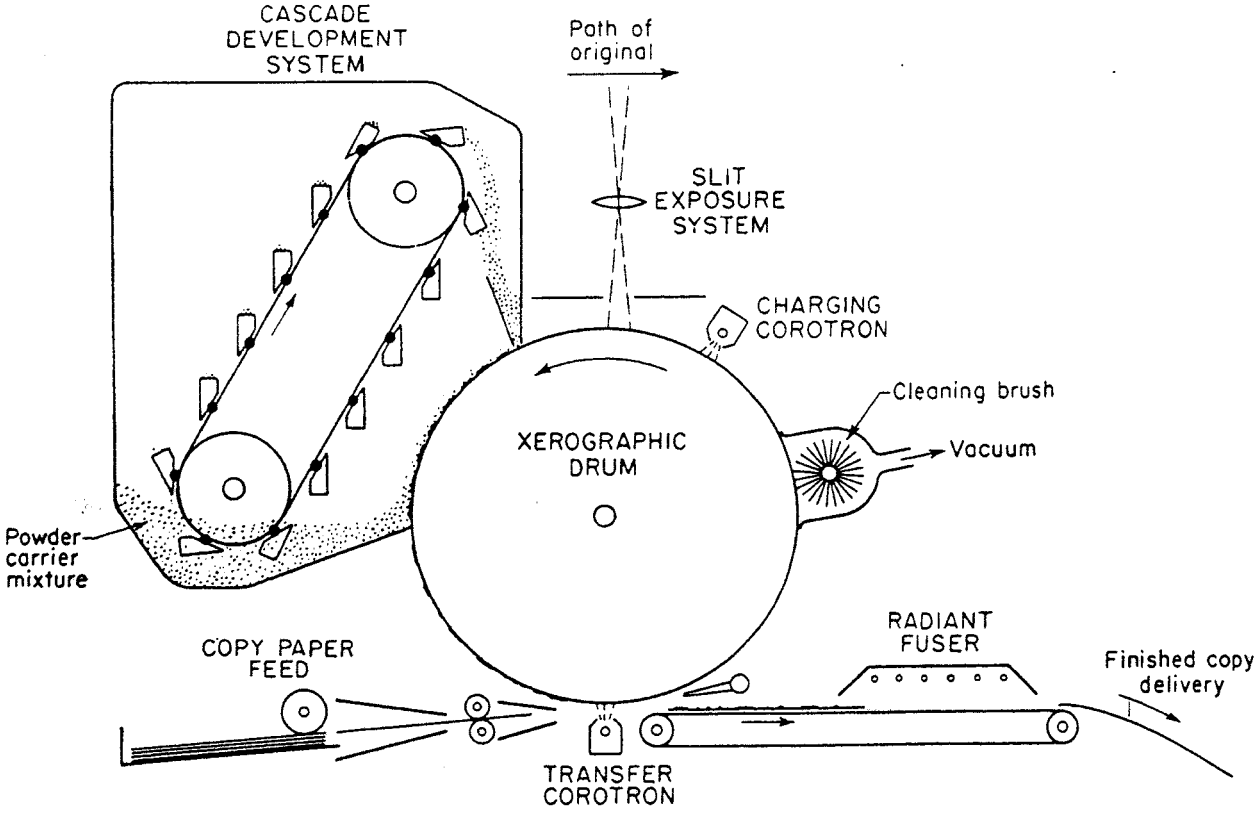

Fig. 7.4. Automatic xerographic copying equipment makes use of the photoconducting property of amorphous selenium plated on the xerographic drum. The selenium holds a positive electrostatic charge in the dark (but allows it to be dissipated when exposed to light). The revolving drum is sensitized through exposure by contact, by projection, or in a camera. The latent image is on the positively charged drum, which attracts the negatively charged black-powder resinous carrier mixture. This resinous pigment is then heated and passed from the drum to the copy paper on which the image is fused.

Table 7.3 Office Copying Processes

Process	Manufacturer	Paper	Copies per minute	Copies Colors	Size Reduction
Electrostatic	IBM	Plain	75	Yes	Yes
Xerographic	Xerox	Plain	10–75	Yes	Yes*
Electrophotographic	Kodak	Plain	70	Yes	Yes*
Xerographic	3M	Plain	25	Yes	No
Electrostatic	3M	Coated	15	Yes	No
Dry toner–dual component	Sharp	Plain	25	Yes	No
Liquid-toner transfer	Savin	Plain	30	Yes	No
Thermal	Heyer	Coated	8–15	No	No
Electrofax	Albin Ind.	Coated	13	Yes	No

*Some models can reduce size.

SOURCE: *The Office* 94 (1) 121 (1981).

for historical records and newspapers in permanent files to conserve space. Such uses have brought about a revolution in *microforms*. Microfilm normally has a reduction of 12 to 22 diameters of the original copy. The resolving power is well over 100 lines/mm, and emulsions capable of resolving 500 lines/mm are being developed. The film itself has a slow-speed panchromatic silver emulsion on a cellulose acetate base. Duplication of the microfilm negative can be by contact printing for a positive reproduction or by negative-to-negative printing. *Microfiche* is the name applied to single-sheet forms of microfilms.

Kalvar film is used for positive copies. When it is exposed, gas bubbles of nitrogen are created which scatter the light. On heat development, the nitrogen develops high pressure which blows air sacs that are 0.5 to 2 μm in diameter. Ultraviolet light stabilizes the compound and the air sacs then scatter the light when the film is projected. It is often used for microfilm (either roll or sheet) duplication.

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Chapter 8

Surface-Coating Industries

Products of the surface-coating industries are essential for the preservation of all types of architectural structures, including factories, from ordinary attacks of weather. Uncoated wood and metal are particularly susceptible to deterioration, especially in cities where soot and sulfur dioxide accelerate such action. Aside from their purely protective action, paints, varnishes, and lacquers increase the attractiveness of manufactured goods, as well as the aesthetic appeal of a community of homes and their interiors. Coatings that are used to cover buildings, furniture, and the like are referred to as trade sales or architectural coatings in contrast to industrial coatings which are used on materials being manufactured. Industrial finishes are applied to a wide variety of materials, such as metal, textiles, rubber, paper, and plastics, as well as wood. Architectural coatings are usually applied to wood, gypsum wallboard, or plaster surfaces.

HISTORICAL. The surface-coating industry is indeed an ancient one; in fact, Noah was told to use pitch within and without the Ark. The origin of paints dates back to prehistoric times when the early inhabitants of the earth recorded their activities in colors on the walls of their caves. These crude paints probably consisted of colored earths or clays suspended in water. The Egyptians, starting very early, developed the art of painting and by 1500 B.C. had a large number and wide variety of colors. About 1000 B.C. they discovered the forerunner of our present-day varnishes, usually naturally occurring resins or beeswax were the film-forming ingredient. Pliny outlined the manufacture of white lead from lead and vinegar, and it is probable that his ancient procedure resembles the old Dutch process.

USES AND ECONOMICS. The manufacture of surface coatings is big business with sales near $10,000 million yearly. No one company has over 10 percent of the market, and there are between 1000 and 1200 companies vying for business. Table 24.1 shows the current and projected size of the market. More than 70 percent of the trade sale paints are water-based.

PAINTS[1]

Historically, surface coatings have been divided into paints (relatively opaque solid coatings applied as thin layers, whose films were usually formed by polymerization of a polyunsatu-

[1]ECT, 3d ed., vol. 16, 1982, pp. 742–761; Weismantel, *Paint Handbook*, McGraw-Hill, New York, 1981.

Table 8.1 Production of Coatings in the United States (in millions of liters and dollars)*

	1979		1995	
	Volume	Value	Volume	Value
Trade sales (architectural)	1695	$3202	2440	$9 325
Industrial	1375	2545	2070	9 055
Special purpose	510	1303	1040	6 440
Total	3580	7050	5550	24 820

*Includes powder coatings

SOURCE: *Chem. Bus.*, October 19, 1981, p. 11

rated oil), varnishes (clear coatings), enamels (pigmented varnishes), lacquers (films formed by evaporation only), printing inks, polishes, etc. These classifications have been most useful in the past, but the introduction of plastic resins into the industry has made such classifications relatively meaningless.

Table 8.2 lists the most important types of ingredients currently used in surface coatings.

CONSTITUENTS. Liquid paint is a dispersion of a finely divided pigment in a liquid. It is composed of a resin or binder and a volatile solvent. The liquid portion is known as the vehicle. The constituents of paints are outlined in Tables 24.2 and 24.3. The pigment, although usually an inorganic substance, may also be a pure, insoluble organic dye known as a toner or an organic dye precipitated on an inorganic carrier such as aluminum hydroxide, barium sulfate, or clay, thus constituting a lake. Pigment extenders, or fillers, reduce the cost of paint and frequently increase its durability. The function of pigments and fillers is not to provide simply a colored surface, pleasing for its aesthetic appeal, important as that may be. The solid particles in the paint reflect many of the destructive light rays, and thus help to prolong the life of the paint. In general, pigments should be *opaque* to ensure good covering power and chemically inert to secure stability, hence long life. Pigments should be nontoxic, or at least of very low toxicity, to both the painter and the inhabitants. Finally, pigments must be wet by the film-forming constituents and be of low cost. Different pigments possess different covering power per unit weight.

Although oils often serve as part of the vehicle for the carrying of pigments, their chief function is to form, or to help form, the protective film and to plasticize it. Without film-forming materials, the pigments would not cling to the surface. Oil paint films are formed

Table 8.2 Paint Constituents

Vehicles
- A. Nonvolatile
  1. Solvent based: oils and/or resins plus driers and additives
  2. Lacquers: cellulosics, resins, plasticizers, additives
  3. Water based: styrene-butadiene, polyvinyl acetate, acrylic, other polymers and emulsions, copolymers plus additives
- B. Volatile
  Ketones, esters, acetates, aromatics, aliphatics

Pigments
- Opaque, transparent, special-purpose types

SOURCE: Weismantel, *Paint Handbook*, McGraw-Hill, New York, 1981, p. 3-3

by the "drying" of various unsaturated oils. These are further described in Chap. 28. The drying is a chemical change involving oxidation and polymerization; it is hastened by pretreatment of the oil and by adding driers, or catalysts, predominantly heavy metallic soaps, which are oxygen carriers usually soluble in oil. These driers need be used only in small amounts (1 to 2% by weight). Reactive oils, such as linseed, soybean, castor, safflower, and tung, are used.

The film-forming nonvolatile portion of the vehicle may be a synthetic resin instead of a drying oil. These synthetic drying oils are known as alkyds and may be made from fatty acids or oils, polybasic acids, and polyhydric resins. Many paints contain both natural and synthetic drying oils. The drying or the hardening of these oils involves chemical reactions, which are rather complex but include oxidation as the initiating step. Some polymerization also occurs and much cross-linkage. Oils which dry to a film possess olefinic unsaturation. For example, the acids of linseed oil contain about 9% saturated acids (palmitic and stearic), 19% oleic acid, 24% linoleic acid, and 48% linolenic acid. In drying, these oils first absorb oxygen from the air, forming peroxides or hydroperoxides at the olefinic bonds. These still-liquid products partly decompose, giving volatile oxidation products, but mainly change in the next stage of the reactions by cross-linkages into the solid, though still elastic, films through colloidal aggregation. In the case of linseed oil, the solid, insoluble, elastic film is called linoxyn. Such films are not permanent, since the chemical reactions continue, though at a much slower rate, until after the course of years the film is entirely destroyed. Light, particularly ultraviolet, catalyzes these reactions, and one of the functions of the pigment in surface coatings is to reflect the light and thus help preserve the film.

Drying oils are seldom used unmodified.[2] They may be improved in a number of different ways by (1) the action of driers (i.e., drying catalysts or promoters), (2) oil bodying, (3) fractionation and segregation, (4) isomerization or conjugation, (5) dehydration, and (6) other carbon double-bond reactions. There are also copolymer oils, poly alcohols such as polypentaerythritol, oil-modified alkyds, and synthetic oils. Bodied oils vary with the oil, but generally have better drying, wetting, and color retention properties than unbodied oils. Bodying is an oxidation reaction and may be achieved either by heating in kettles or by blowing air in fine bubbles through the oils at 100 to 200°C for several hours. Solvent or liquid-liquid extraction separates the drying constituents of an oil from the nondrying constituents. The isomerization of paint oils, especially popular for linseed and soybean oils, involves partial rearrangement of the isolated, nonconjugated double bonds into more reactive conjugated positions upon heat treatment with catalysts, such as certain metal oxides, activated nickel, or SO_2. Dehydration, at present, is applicable only for castor oil and is achieved by heating the oil in a vacuum in the presence of dehydrating catalysts such as alumina, fuller's earth, silica gel, H_3PO_4, or H_2SO_4.

In emulsion-base paints, the film-forming materials are the various latices with or without other additions. Film formation takes place largely through coalescence of dispersed resin particles to form a strong continuous film. The vehicle for this class of paints is an emulsion of binder in water; the binder may be oil, an acrylic or polyvinyl acetate resin, or another emulsifiable binder. Although water-thinned paints date back to antiquity, they were not commercially important until casein-based paints were developed about 1925. Their phenomenal growth is indicated by the large increase in U.S. production. Resin-emulsion paints have been widely used since World War I, but latex-based paints, introduced commercially in 1948, have had spectacular growth; more than 70 percent of interior paint sales are this type. This type of paint was developed to meet demands for greater ease of application, quick

[2]Mattil, Short Course on Drying Oils, *J. Am. Oil Chem. Soc.* 36 477 (1959).

drying, low odor, easy cleaning, great durability, and impermeability to dirt. Latex paints have as their major film-forming constituent a synthetic resin latex, with or without other film-forming constituents added, in an oil-water emulsion-type system. The continuous phase consists of an alkali-dispersed hydrophilic colloid in water and contains two or more different types of particles in suspension.

Styrene–butadiene rubber (SBR) copolymer was the original quality film-former in latex paint. Polyvinyl acetate (PVA), acrylics, and PVA-acrylic copolymers have largely replaced SBR as film formers in today's trade. Quality is substantially improved.

Proper paint formulation centers around the specific requirements of the particular application. These requirements are hiding power, color, weather resistance, washability, gloss, metal anticorrosive properties, and consistency, as related to type of application (brushing, dipping, spraying, or roller coating). Individual requirements are met by proper choice of pigments, extenders, and vehicles by the paint formulator. Since the techniques of paint technology formulation are still largely empirical, it is difficult to predict the properties of a specific formulation, and this often means that a considerable number of trials have to be run before the desired properties are obtained. However, by using simple statistical methods, it has been demonstrated that more efficient testing and development results are obtainable. Almost all the major paintmakers have developed some type of automated color-control system; new methods reduce the time required to match paint and, by giving closer control of pigment requirements, keep production costs down.[3]

For the modern paint formulator, some authorities believe the most important concept is that of pigment volume concentration (PVC). It is defined as:

$$\text{PVC} = \frac{\text{volume of pigment in paint}}{\text{volume of pigment in paint} + \text{volume of nonvolatile vehicle constituents in paint}}$$

The PVC largely controls such factors as gloss, reflectance, rheological properties, washability, and durability. The inherent vehicle requirements of the pigment-extender combination being applied, however, affect the PVC used in a given formulation. As a consequence there is usually a range of PVC for a given paint, as indicated in the following tabulation:

Flat paints	50–75%	Exterior house paints	28–36%
Semigloss paints	35–45%	Metal primers	25–40%
Gloss paints	25–35%	Wood primers	35–40%

The PVC of a given formulation serves as the guide for reformulation work, using different pigment or vehicle combinations, and as such is extremely useful to the paint formulator. The addition of pigment continues to reinforce and improve the film-forming properties until a critical concentration (CPVC) is reached. At this point and beyond, the resistance properties of the paint decrease, as the film becomes porous, causing the paint to weather faster and lose abrasion resistance and flexibility.[4]

MANUFACTURING PROCEDURES. The various operations needed to mix paints are wholly physical. These unit operations are shown in proper sequence in the flowchart in Fig. 8.1

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[3]Color Technology, *Chem. Eng.* 75 (17) 146 (1968).

[4]Weismantel, Paints and Coatings for CPI Plants and Equipment, *Chem. Eng.* 88 (8) 130 (1981); Rowland, Graphical Solution to CPVC Problems in Latex Paints, *J. Coat. Technol.* 54 (686) 51 (1982).

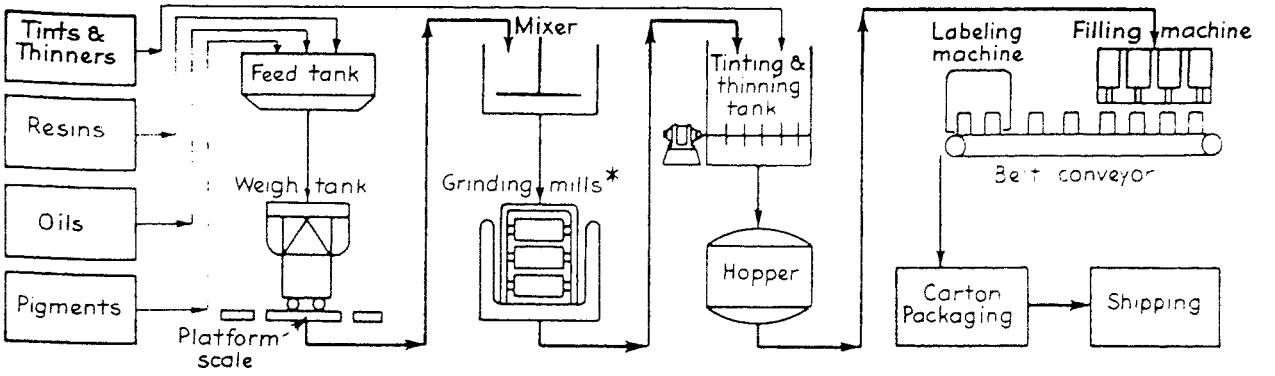


Fig. 8.1. Flowchart for the mixing of paint. NOTE: Because a complete paint factory consumes upward of 2000 different raw materials and produces ten times as many finished products, it is not possible to give yields, etc.

**Many types of grinding mills are used in the same plant, either in series or in parallel. Some of them are ball mills, high-speed dispersers, and three- and five-roll steel mills*

Chemical conversions are involved in the manufacture of the constituents of paints as well as in the drying of the film. The manufacturing procedures illustrated are for a mass-production paint. The weighing, assembling, and mixing of the pigments and vehicles take place on the top floor. The mixer may be similar to a large dough kneader with sigma blades. The batch masses are conveyed to the floor below, where grinding and further mixing take place. A variety of grinding mills may be used. One of the oldest methods is grinding, or dispersion, between two buhrstones; however, ball-and-pebble mills and steel roller mills were the principal grinding mills used until recently. Sand mills, high-speed agitators, and high-speed stone mills are being used increasingly to grind paint and enamels. The types of pigments and vehicles are dominant factors in the choice of equipment used (Figs. 8.2 and 8.3).

The mixing and grinding of pigments in oil require much skill and experience to secure a smooth product without too high a cost. Perry[5] presents these operations in a useful manner, with pictures of various mills and tabulations of the engineering factors concerned. No one machine is universally applicable.

After mixing, the paint is transferred to the next-lower floor, where it is thinned and tinted in agitated tanks, which may hold batches of several thousand liters. The liquid paint is strained into a transfer tank or directly into the hopper of the filling machine on the floor below. Centrifuges, screens, or pressure filters are used to remove nondispersed pigments. The paint is poured into cans or drums, labeled, packed, and moved to storage, each step being completely automatic.

For latex paints, the dispersant and ammonia are added to water in a pony mixer, followed by pigments premixed and ground in a ball mill. The pigments and extenders most used are water-dispersible grades of titanium dioxide, zinc sulfide, lithopone, and regular grades of barium sulfate, mica, diatomaceous silica, clay, and magnesium silicate. A combination of four or five inerts is generally employed. The usual colored pigments may be used for tinting, with certain exceptions such as prussian blue, chrome yellow, chrome green, and carbon black. The first three are sensitive to alkalies, and the last tends to break the emulsion. Also, sodium-free alkalies and pigments are preferred, since they minimize efflorescence caused by sodium sulfate on the paint surface. Interior pigments must, by law, be nonpoisonous if

[5]Perry, 5th ed., p. 8–42 for roller mill and pigment grinding, p. 19–24 for kneaders, p. 5–25 for ball mills, and p. 8–8 for principles of size reduction.

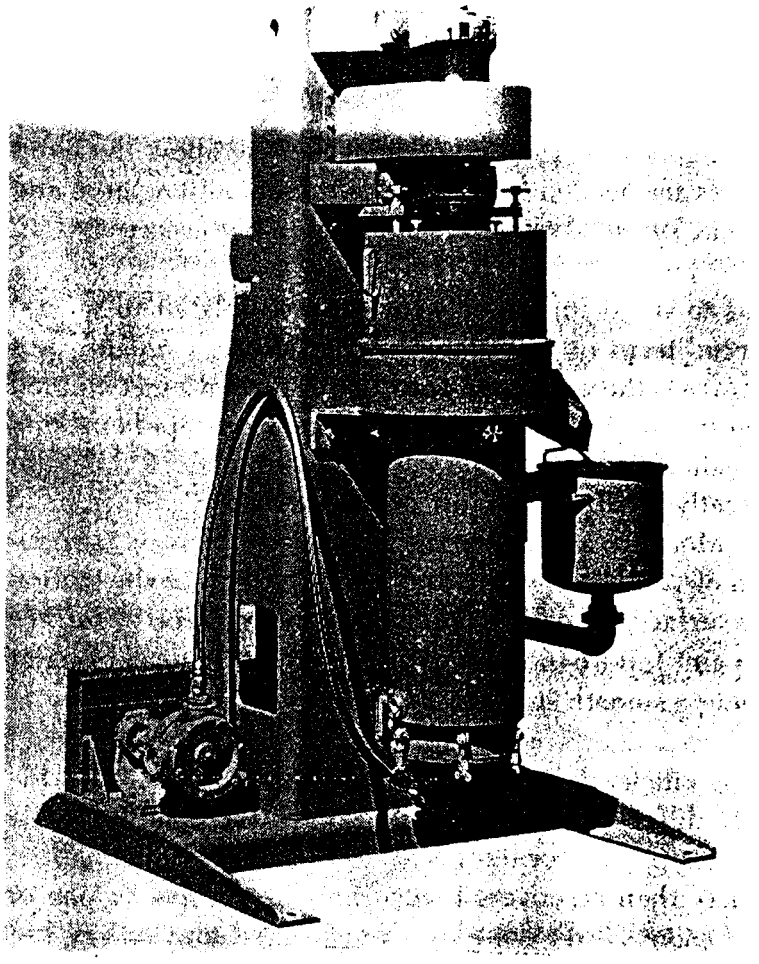


Fig. 8 .2. A sand-grinding mill, illustrating the process and apparatus developed by DuPont. This mill is a combination type, with round grains of Ottawa sand which grind and disperse the pigments in the medium grinding chamber, followed by a screen which holds back the sand.

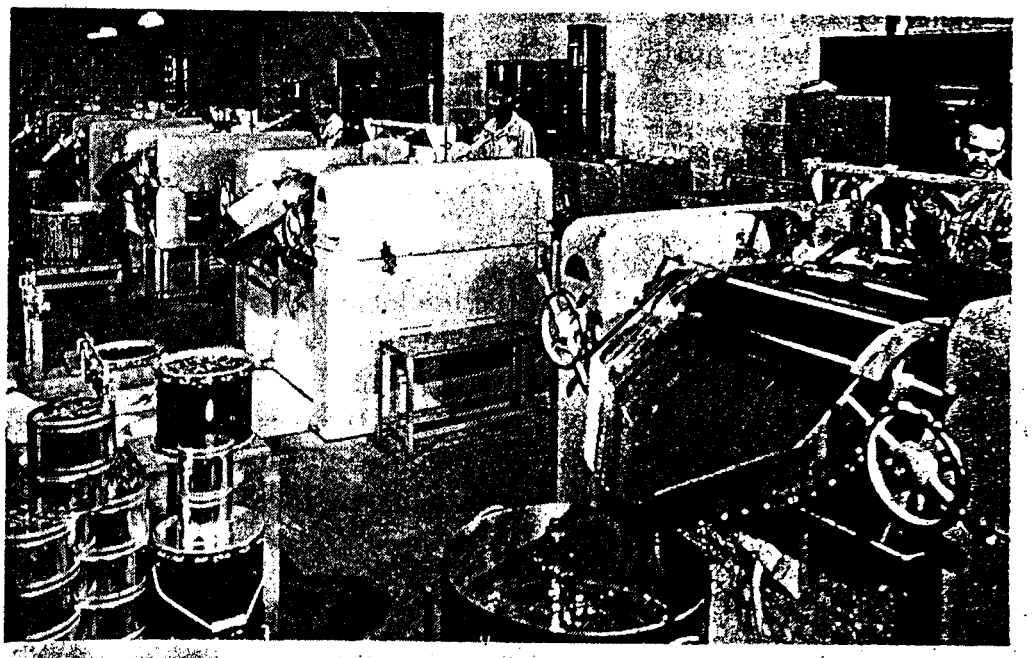


Fig. 24.3. Three-roll mill. *(J. H. Day Co.)*

ingested. The film formers are added to the pigment dispersion, followed by a preservative solution (usually chlorinated phenols) and an antifoam (sulfonated tallow or pine oil). The latex emulsion is stirred in slowly, followed by water. The paint is mixed, screened, and mixed again before packaging. A typical paint consists of 35% pigment and filler and about 21% film-forming ingredients. Latex paints require the addition of thickeners to allow the paint to be spread satisfactorily. Other additives are needed for specific purposes: antibacterial and antimildew agents, freeze-thaw stabilizers, surfactants, defoamers, and pH adjusters.

PAINT FAILURE. The failure of paints to stand up under wear may be related to several causes, and in each case there is a special term used to describe the failure. *Chalking* is a progressive powdering of the paint film from the surface inward that is caused by continued and destructive oxidation of the oil after the original drying of the paint. Very rapid chalking is termed *erosion*. *Flaking*, sometimes called *peeling*, is due to poor attachment of the paint to the surface being covered and is usually attributed to dirt or grease on the surface or to water entering from behind the paint. Moisture accumulation underneath paint is particularly destructive. *Alligatoring* is a form of peeling in which the center portion of the section starting to peel remains attached to the surface. *Checking* denotes a very fine type of surface cracking. As opposed to these types of paint failure, normal wear is gradual removal of paint from the surface by the elements, leaving a smooth surface.

PAINT APPLICATION. A surface that is efficiently painted, varnished, or lacquered often requires the application of a number of different coatings varied to suit the condition. For example, most surfaces require the use of a primer, or filler coat, to smooth over inequalities and to secure better adherence. This may then be covered with the paint proper in one or more applications. Much application of paint is still done by hand brushes and rollers, but dipping and spray painting are gaining favor because of the ease and rapidity of spread, thus saving labor, though wasting a little material. The use of electric charges greatly reduces spray paint loss. A wide variety of atomizers for spraying is available, including internal mixing and the more common external mixing. Spray guns are operated frequently at pressure of 275 to 414 kPa. Coating materials in aerosol containers, sold in millions, are popular because of their convenience of application. Prefinishing of metal and wood sheets is done by reverse or direct roll coating at the factory. This process is more economical than painting on the job, and the finishes are of better quality.

PIGMENTS[6]

Pigments[7] (Table 8.3) are colored, organic and inorganic insoluble substances used widely in surface coatings, but they are also employed in the ink, plastic, rubber, ceramic, paper, and linoleum industries to impart color. A large number of pigments and dyes are consumed because different products require a particular choice of material to give maximum coverage, economy, opacity, color, durability, and desired reflectance. White lead, zinc oxide, and lithopone were once the principal white pigments; colored pigments consisted of prussian blue.

[6]ECT, 3d ed., vol. 17, 1982, pp. 788–889; Patton, *Pigment Handbook*, Wiley, New York, 1973.

[7]Specifications for pigments, ASTM Standards, vol. 8, 1982.

***Table* 8.3** Pigments and Extenders for Surface Coatings

Ingredients		Function
Pigments		
White hiding pigments	Yellow pigments	To protect the film by reflecting the destructive ultraviolet light, to strengthen the film, and to impart an aesthetic appeal. Pigments should possess the following properties: opacity and good covering power, wettability by oil, chemical inertness, nontoxicity or low toxicity, reasonable cost
Titanium dioxide	Litharge	
Zinc oxide	Ocher	
Lithopone	Lead or zinc chromate	
Zinc sulfide	Hansa yellows	
Antimony oxide	Ferrite yellows	
Black pigments	Cadmium lithopone	
Carbon black	Orange pigments	
Lampblack	Basic lead chromate	
Graphite	Cadmium orange	
Iron black	Molybdenum orange	
Blue pigments	Green pigments	
Ultramarine	Chromium oxide	
Copper phthalocyanine	Chrome green	
Iron blues	Hydrated chromium oxide	
Red pigments	Phthalocyanine green	
Red lead	Permansa greens (phthalocyanine blue plus zinc chromate)	
Iron oxides	Brown pigments	
Cadmium reds	Burnt sienna	
Toners and lakes	Burnt umber	
Metallics	Vandyke brown	
Aluminum	Metal protective pigments	
Zinc dust	Red lead	
Bronze powder	Blue lead	
	Zinc, basic lead, and barium potassium chromates	
Extenders or Inerts		
China clay	Gypsum	To reduce the pigment *cost* and in many cases to increase the covering and weathering power of pigments by complementing pigment particle size, thus improving consistency, leveling, and settling
Talc	Mica	
Asbestos (short fibers)	Barite, barium sulfate	
Silica and silicates	Blanc fixe	
Whiting		
Metal stearates		

lead chromates, various iron oxides, and a few lake colors. Today titanium oxide in many varieties is almost the only white pigment used. Lead pigments, formerly of major importance, are now prohibited by law for many uses.

White Pigments

The oldest and formerly most important of the white pigments is white lead, which is no longer permitted as a constituent of most paints. Zinc oxide, another white pigment formerly widely used, is now of only minor importance. Table 8.4 presents a summary of the characteristics of white pigments.

LITHOPONE. Lithopone is a mixed zinc sulfide–barium sulfate pigment that contains about 30% zinc sulfide. The original light sensitiveness has been overcome by raw material purification and by the addition of such agents as polythionates and cobalt sulfate. Lithopone is a

Table 8.4 Comparison of White Pigments

	Titanium Dioxide			White Lead Basic Lead
	Anatase	Rutile	Zinc Oxide	Carbonate
Refractive index	2.55	2.70	2.08	2.0
Average particle size, μm	0.2	0.2–0.3	0.2–0.35	1.0
Density, g/cm^3	3.8–4.1	3.9–4.2	5.6	7.8–6.9
Oil absorption, grams of oil/100 g pigment	18–30	16–48	10–25	11–25
Relative hiding power	100	125–135	20	15
Price (1981), $ per kilogram	1.51	1.65	1.03	1.54

brilliantly white, extremely fine, cheap, white pigment. It is particularly well adapted to interior coatings.

The manufacture is shown diagrammatically in Fig. 8.4 where the barium, zinc, and lithopone circuits are represented by different types of lines. The barium sulfide solution is prepared by reducing barite ore ($BaSO_4$) with carbon and leaching the resulting mass. The equation is:

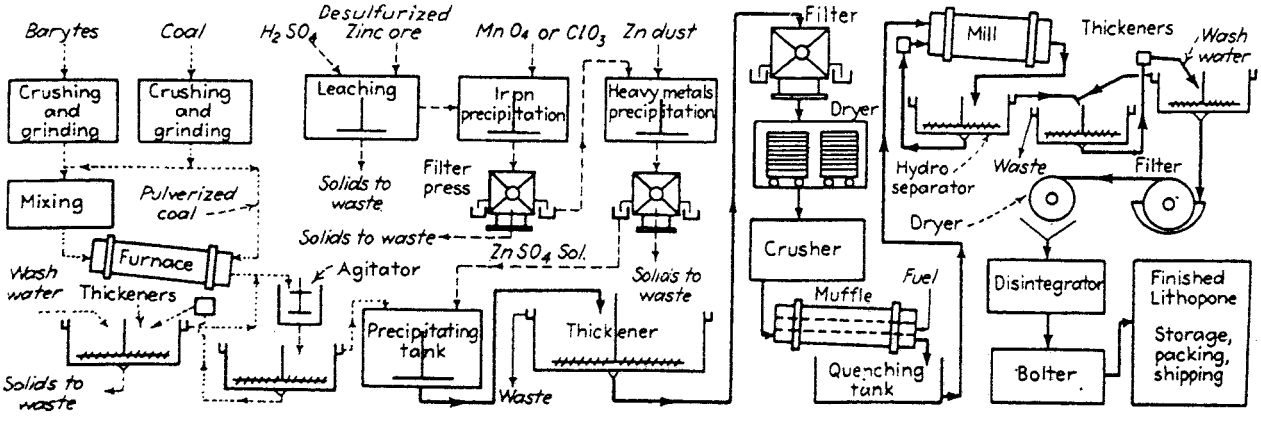
$$BaSO_4 + 4C \rightarrow BaS + 4CO$$

Scrap zinc or concentrated zinc ores are dissolved in sulfuric acid, and the solution purified as shown. The two solutions are reacted, and a heavy mixed precipitate results which is 28 to 30% zinc sulfide and 72 to 70% barium sulfate.

$$ZnSO_4 + BaS \rightarrow ZnS + BaSO_4$$

This precipitate is not suitable for a pigment until it is filtered, dried, crushed, heated to a high temperature, and quenched in cold water. The second heating in a muffle furnace at 725°C produces crystals of the right optical size.

Lithopones are used in water-based paints because of their excellent alkali resistance. They



In order to produce 1 t of lithopone, the following materials and utilities are needed:

Barytes	0.85 t	Zinc ore (60% zinc)	0.4 t
Coal (half for steam)	1.1 t	H_2SO_4 (50°Bé)	0.5 t
Electricity	400 MJ	Direct labor	15 work-h

Fig. 8.4. Flowchart for lithopone manufacture. - - - - - - - - indicates the barium circuit, - - - - - - the zinc circuit, and ——— the lithopone circuit.

are also used as a whitener and reinforcing agent for rubber and as a filler and whitener for paper.

TITANIUM DIOXIDE. The most important white pigment is TiO_2. It is marketed in two crystalline forms, anatase and the more stable rutile. Almost all the TiO_2 used in paints is the rutile form. Anatase can be converted to rutile by heating to 700 to 950°C. TiO_2 is widely employed in exterior paints and also in enamels and lacquers. A typical exterior white paint contains about 60% pigment, of which 20% is TiO_2, 60% talc, and 20% mica. Such a formulation has long life through controlled chalking (a layer of loose pigment powder on the surface of the paint film, which acts as a self-cleaner for the paint) and presents a good surface for subsequent repainting. About 50 percent of this pigment is consumed in paints, varnishes, and lacquers and the second most important customer (23 percent) is the paper industry. Another important use is in the coloring of plastics. Demand in 1981 was 750,000 t.[8,8a]

The two important methods for producing TiO_2 are the sulfate and chloride processes. The sulfate is the older process, but the chloride process has largely supplanted it and produces over 60 percent of the U.S. production. The sulfate process uses the cheaper, domestic ore, ilmenite, as a raw material, while the chloride process requires the more expensive imported ore, rutile. Ilmenite can be converted to synthetic rutile, and DuPont has a patented chloride process that uses ilmenite.

The sulfate process has traditionally used batch ore digestion in which concentrated sulfuric acid is reacted with ilmenite. This reaction is very violent and causes the entrainment of SO_x and H_2SO_4 in large amounts of water vapor; they are subsequently emitted to the atmosphere in far larger quantities than are allowed by clean air standards. In an effort to reduce the particulate emissions, scrubbers have been installed at most plants, but these, in turn, have necessitated the treatment of large quantities of scrubbing liquid before discharge. Other waste-disposal problem products are spent sulfuric acid and copperas ($FeSO_4 \cdot 7H_2O$).

The chloride process utilizes the treatment of rutile (natural or synthetic) with chlorine gas and coke to produce titanium tetrachloride. The titanium tetrachloride is distilled to remove impurities and then reacted with oxygen or air in a flame at about 1500°C to produce chlorine and very fine-particle titanium dioxide. The chlorine is recycled (Fig. 8.5). The waste products are easier to dispose of than those formed by the sulfate process.

A new sulfate process that claims to eliminate many of the old pollution problems has been introduced by NL Industries.[9] This is a continuous process using relatively dilute sulfuric acid

[8]*Chem. Week* 130 (26) 43 (1982).

[8a]t = 1000 kg.

[9]Kaplan, Improved Titanium Dioxide Process Keeps Plant Alive, *Chem. Eng.* 89 (12) 86 (1982).

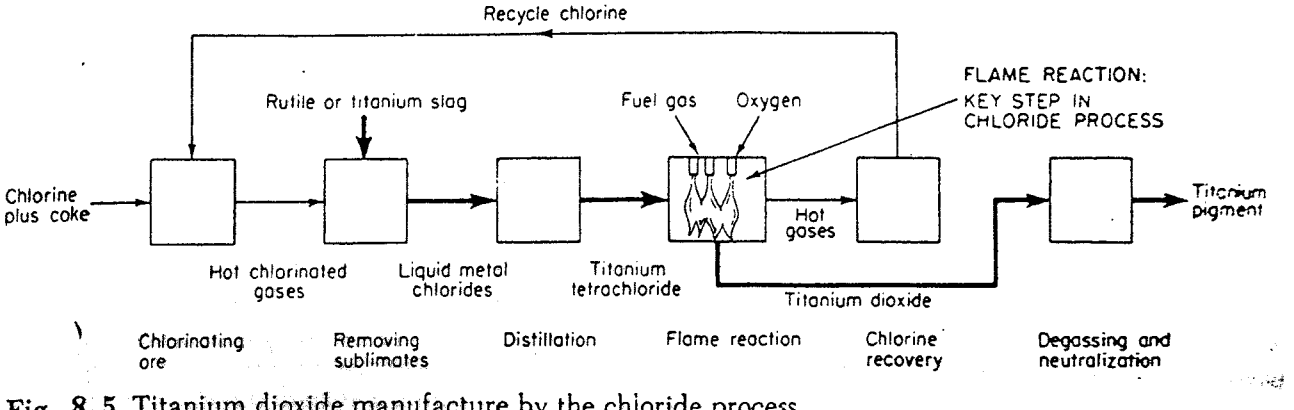


Fig. 8.5. Titanium dioxide manufacture by the chloride process.

(25 to 60%) to temper the violent, original reaction and reduce the amount of water-vapor-entrained particulates. As the process uses more dilute acid than the older batch process, more of the spent acid can be recycled. Flow diagrams for both the batch and continuous processes are shown in Fig. 24.6.

$$TiO_2(ore) + H_2SO_4 \longrightarrow TiOSO_4 + FeSO_4 \cdot H_2O$$

$$TiOSO_4 + H_2O \longrightarrow TiO_2 \cdot xH_2O$$

$$TiO_2 \cdot xH_2O \xrightarrow[800\text{–}1000°C]{\text{heat}} TiO_2$$

The hydrolysis reaction is dependent upon many factors: quantity and quality of the seeds added to the colloidal suspension of TiO_2, concentration, rate of heating, and pH. Introduction of seeds prior to hydrolysis ensures production of the desired form. Using anatase seeds, 6 h of boiling is needed, and with rutile seeds, the time can be shortened to 3 h.

BARIUM SULFATE. Barium sulfate, often prepared by grinding the ore barite, is not usually used alone as a white pigment because of its poor covering power, but is widely used as a pigment extender. It also contributes to gloss. Its principal use (over 90 percent) is in oil-drilling muds. Only 3 percent of U.S. production is used in paints. Blanc fixe is made by precipitation of a soluble barium compound, such as barium sulfide or barium chloride, by a sulfate. This form has finer particles than the ground barite and is often used in printing inks to impart transparency.

Black Pigments

The only major black pigments are the carbon blacks. These come in various shades and their manufacture is discussed under industrial carbon in Chap. 8. Lampblack, which has a larger particle size, is used for tinting to produce shades of gray. The carbon blacks are very opaque and have excellent durability, resistance to all types of chemicals, and lightfastness. They

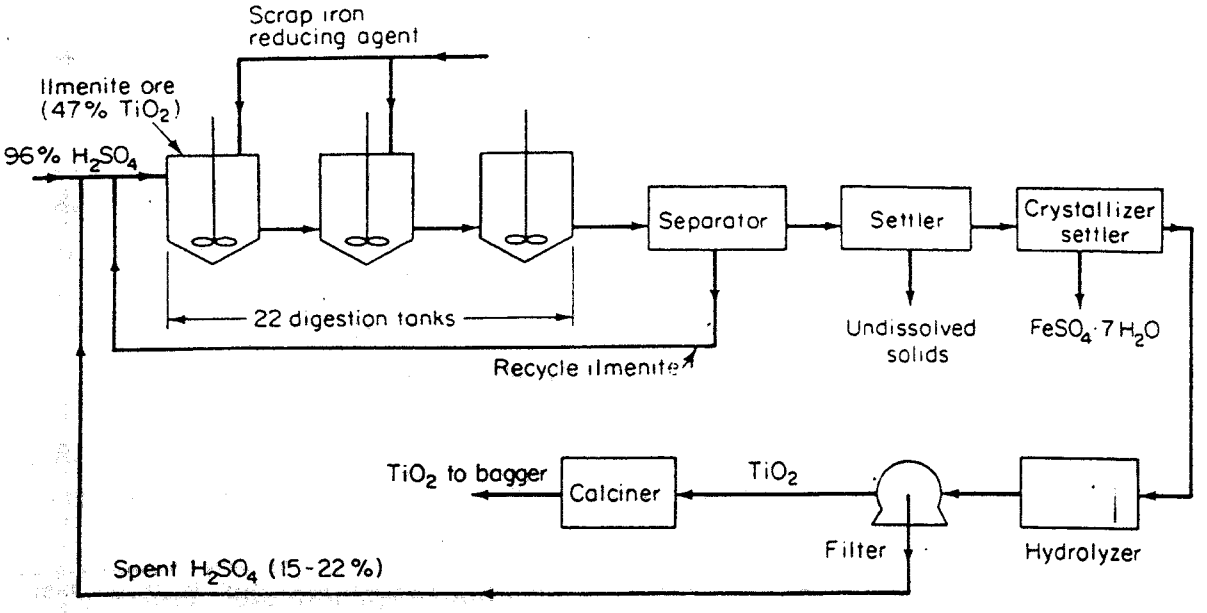


Fig. 8.6. Titanium dioxide manufacture by two types of sulfuric acid processes.

should not be used in direct contact with iron and steel in primer coatings because they stimulate metal corrosion.

Blue Pigments

ULTRAMARINE BLUE. This is a complex sodium aluminum silicate and sulfide made synthetically. Because it has a sulfide composition, it should not be used on iron or mixed with lead pigments. Ultramarine is widely used as bluing in laundering to neutralize the yellowish tone in cotton and linen fabrics. It is also applied for whitening paper and other products. Special grades, low in free sulfur, are used in inks.

PHTHALOCYANINE BLUES. This group of blues, marketed in the United States since 1936, is particularly useful for nitrocellulose lacquers in low concentrations as a pigment highly resistant to alkalies, acids, and color change. For details of manufacture, see Chap. 39. As presently produced, they are most stable pigments, resistant to crystallization in organic solvents, and essentially free from flocculation in coatings. Both the greens and the blues have high tinting power and are used in latex paints and in printing inks, as well as all types of interior and exterior coatings. They are prepared by reacting phthalic anhydride with a copper salt with or without ammonia.[10]

FERROCYANIDE BLUES. These blues are known as prussian blue, chinese blue, milori blue, bronze blue, antwerp blue, and Turnbull's blue. As these names have lost much of their original differentiation, the more general term *iron blues* is preferred. These pigments are made in essentially the same manner by the precipitation of ferrous sulfate solutions (sometimes in the presence of ammonium sulfate) with sodium ferrocyanide, giving a white ferrous ferrocyanide, which is then oxidized to ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, or to $Fe(NH_4)[Fe(CN)_6]$ by different reagents such as potassium chlorate, bleaching powder, and potassium dichromate. The pigment is washed and allowed to settle, since filtration is extremely difficult because of its colloidal nature. Iron blues possess very high tinting strength and good color performance; their relative transparency is an advantage in dip-coating foils and bright metal objects, and for colored granules for asphalt shingles. They cannot be used in water-based paints because of their poor alkali resistance.

Red Pigments

RED LEAD. Red lead (Pb_3O_4) has a brilliant red-orange color, is quite resistant to light, and finds extensive use as a priming coat for structural steel because it possesses corrosion-inhibiting properties. Red lead, or minium, is manufactured by the *regular process* by oxidizing lead to litharge (PbO) in air and further oxidizing the litharge to red lead. In the *fumed* process, which produces smaller particles, molten lead is atomized by compressed air and then forced through the center of a gas flame, which in turn converts it into litharge as a fume collected in filter bags. The litharge is then oxidized to red lead by roasting in air.

FERRIC OXIDE (Fe_2O_3). This is another red pigment employed in paints and primers, as well as in rubber formulation. A wide range of natural red oxide pigments is available and, because

[10] *Tech. Bull.* 902, Am. Cyanamid Co.

of durability, they are used in barn and freight-car paints. Synthetic pigment is made by heating iron sulfate. Venetian red is a mixture of ferric oxide with up to an equal amount of the pigment extender, calcium sulfate. This pigment is manufactured by heating ferrous sulfate with quicklime in a furnace. Venetian red is a permanent and inert pigment, particularly on wood. The calcium sulfate content, which furnishes corrosion-stimulating sulfate ions, disqualifies this pigment for use on iron. Indian red is a naturally occurring mineral whose ferric oxide content may vary from 80 to 95%, the remainder being clay and silica. It is made by grinding hematite and floating off the fines for use. *Magnetic* iron oxides have acquired a new market in the production of magnetic tapes for computers and audio and video recorders. The pigment and colorant market utilizes 48 percent of production and magnetic and electronic applications, 11 percent.[11]

OTHER REDS. *Basic lead chromate* $PbCrO_4 \cdot Pb(OH)_2$ may also be used as an orange-red pigment; it is an excellent corrosion inhibitor. It is manufactured by boiling white lead with a solution of sodium dichromate. *Cadmium reds* are made by roasting the precipitate obtained by mixing cadmium sulfate, sodium sulfite, and sodium selenide. Cadmium colors range from light yellow to maroon and are available in pure form as well as in lithopones. The larger the quantity of selenium used, the greater the shift toward red. Red pigments include a large variety of insoluble organic dyes, either in the pure state as toners or precipitated on inorganic bases as lakes. For example *tuscan red* is a name sometimes applied to combinations of red iron oxide pigment and a light-fast organic red pigment used where bright colors are needed for exterior paints. Quinacridones are extremely durable reds, oranges, and violets comparable in serviceability to phthalocyanines.

Yellow Pigments

OCHER. Ocher is a naturally occurring pigment consisting of clay colored with 10 to 30% ferric hydroxide. It must be ground and levigated. At best the ochers are very weak tinting colors and are being replaced by synthetic hydrated yellow iron oxides for brighter color and better uniformity.

CHROME YELLOWS. Yellow pigments with a wide variety of shades fall in the class known as chrome yellows; they are the most popular yellow pigments because of exceptional brilliance, great opacity, and excellent lightfastness. They are produced by mixing a solution of lead nitrate or acetate with a solution of sodium dichromate. Extenders may be present in up to an equal weight of gypsum, clay, or barite. The pigment is of high specific gravity and settles out. The use of chrome pigments is sharply limited by their toxicity when ingested.

ZINC YELLOW. Zinc yellow or chromate, although of poor tinting power, is used because of its excellent corrosion-inhibiting effect both in mixed paints and as a priming coat for steel and aluminum. Zinc yellow is a complex of the approximate composition $4ZnO \cdot K_2O \cdot 4CrO_3 \cdot 3H_2O$. Two other yellow chromate pigments are strontium chromate and barium chromate, both used as corrosion inhibitors.

[11]Brown, Iron Oxide, *Chem. Bus.* June 1, 1981, p. 33.

Green Pigments

PHTHALOCYANINE GREEN. The major green pigment is phthalocyanine green. It is a complex copper compound and has excellent opacity, lightfastness, and chemical resistance. It is suitable for use in both solvent- and water-based paints.

CHROMIUM OXIDE GREEN. One of the oldest green pigments is chromium oxide (Cr_2O_3). It has many disadvantages, such as high cost and lack of brilliancy and opacity. It is made by calcining either sodium or potassium dichromate with sulfur in a reverberatory furnace.

$$Na_2Cr_2O_7 + S \rightarrow Cr_2O_3 + Na_2SO_4$$

GUIGNET'S GREEN. Guignet's green (emerald green) is a hydrated chromic oxide, $Cr_2O(OH)_4$, possessing a much more brilliant green color than the oxide and yet having a good permanency. It is prepared by roasting a mixture of sodium dichromate and boric acid at a dull red heat for several hours. In addition, a green of good permanency for use in outside trim paints may be obtained in intimate mixtures of copper phthalocyanine with zinc chromate or hansa yellow. The brightest permanent green available, chlorinated copper phthalocyanine, is expensive but durable. Water-dispersible grades and pulp colors are available for latex paints.

CHROME GREEN. This pigment is sold under various names and is a mixture or a coprecipitation of chrome yellow and prussian blue. Inert fillers are used with this pigment in making paints. Unless carefully ground or coprecipitated, the two colors may separate when mixed in a paint. Also, because of its lead content, it is being phased out of use. It has poor alkali resistance and cannot be used in latex paints.

Brown Pigments

The carefully controlled heating of various naturally occurring iron-containing clays furnishes the brown pigments known as *burnt sienna, burnt umber*, and *burnt ocher*. The iron hydroxides are more or less converted to the oxides. The umbers contain brown manganic oxide as well as the iron oxides. These are all permanent pigments suitable for both wood and iron; however, the siennas are being replaced as tinting colors by synthetic oxides because of the latter's greater color strength and clarity. *Vandyke brown* is a native earth pigment of indefinite composition, containing oxide of iron and organic matter.

Toners and Lakes

Toners are insoluble organic dyes that may be used directly as pigments because of their durability and coloring power. Lakes result from the precipitation of organic colors, usually of synthetic origin, upon some inorganic base. They are employed in many colors. Some typical examples are: para red is formed by diazotizing *p*-nitroaniline and coupling it with 3-naphthol. Toluidine toner, a better and more expensive red pigment, is made by diazotizing *m*-nitro-*p*-toluidine and coupling it with β-naphthol. Hansa yellow G (lemon yellow) is manufactured by diazotizing *m*-nitro-*p*-toluidine and coupling it with acetoacetanilide. Hansa

yellow 10G (primrose yellow) is made by coupling orthochloroacetanilide with diazotized 4-chloro-2-nitroaniline. Lakes are really dyed inorganic pigments. The inorganic part, or base, consists of an extender such as clay, barite, or blanc fixe and aluminum hydroxide. Either the organic dye may be precipitated onto an already existing base, such as clay or barite suspended in solution, or both the dye and the base may be coprecipitated, e.g., onto blanc fixe or aluminum hydroxide. Both toners and lakes are ground in oil or applied like any other pigment.

Miscellaneous Pigments

In surface coatings, metallic powders, i.e., flaked or finely powdered metals and alloys, have been developed not only for decorative purposes, but also for their durability, heat-reflective properties, and anticorrosion effects. Aluminum flaked powder is usually made by steel-ball milling the granular form in a cylindrical mill to which are added a lubricant and a dispersing agent. Powdered zinc, more often referred to as zinc dust, is used in primers, in paints for galvanized iron, and in finish coats. Lead powders and pastes are used in primers. Though not classed with pigments, one of the uses of metallic stearates is as a pigment-suspending agent. Luminescent paints have a variety of uses, particularly in advertising displays and for aircraft, because of their high visibility.

VARNISHES

A varnish is an unpigmented colloidal dispersion or solution of synthetic and/or natural resins in oils and/or thinners used as a protective and/or decorative coating for various surfaces and which dries by evaporation, oxidation, and polymerization of portions of its constituents. Not being pigmented, varnishes are less resistant to damage by light than are paints, enamels, and pigmented lacquers. They furnish, however, a transparent film, which accentuates the texture of the surface coated. Varnishes are frequently oleoresinous; there are two minor classes, spirit varnishes and japans. Oleoresinous varnishes are solutions of one or more natural or synthetic resins in a drying oil and a volatile solvent. The oil reduces the natural brittleness of the pure-resin film. Spirit varnishes are solutions of resins, but the solvent is completely volatile and nonfilm-forming. Oleoresinous varnishes were formerly of major importance, but alkyd and urethane varnishes have largely replaced them because of greater durability, less yellowing, ease of application, and beauty. Pressure to reduce the amount of air-polluting solvents in varnishes and paints, coupled with the desire for water cleanup of tools and spills, has led to the development of water-thinned varnishes.

Spirit varnishes are solutions of resins in volatile solvents only, such as methanol, alcohol, hydrocarbons, ketones, and the like. Spirit varnishes dry most rapidly but are likely to be brittle and eventually crack and peel off unless suitable plasticizers are added. The preparation of these products involves active stirring, and sometimes heating, to bring about the desired solution. An important example of a spirit varnish is shellac or a solution of the resin shellac in methanol or alcohol. Japans are rarely used now. They are opaque varnishes to which asphalt or some similar material has been added for color and luster. They may be subdivided into baking, semibaking, and air-drying japans, according to their method of application.

For exterior use alkyd resins are the more durable vehicles, whereas modified phenolic

varnishes are used for interior finishes. Their composition varies widely, depending upon cost and end use. Some are applied with a brush, and others are sprayed on the surface. When hardened by baking, they are particularly durable. Alkyd-amine resins are used to improve quality.

RESINS. The original resins used were copals, which consisted of fossil gums from various parts of the world. Another natural but present-day resin widely employed is that from the pine tree, or rosin. When a plant exudes these products, they are called balsams and upon evaporation of the volatile constituents, they yield the resin. Thus the longleaf, yellow, and hard pines of the southern states, under proper incision, yield a balsam which, after distillation, gives turpentine and a residue called rosin. The latter product is essentially abietic acid (Chap. 32). Most of the natural resins employed are fossil resins that have been buried and gradually changed over centuries. From the rosin of the present, these resins[12] reach back through dammar, copal, and kauri resins to the oldest of the fossil resins, amber. Some resins like kauri and copal are so ancient that they have changed to insoluble products and must be partly depolymerized by heat before they can be dissolved or blended with the hot oils and other constituents in the varnish kettle. An important present-day resin is shellac, or lac resin. Unlike the others, it is the product of animal life and comes from a parasitic female insect *(Coccus lacca)* which, when feeding upon certain trees in India, secretes a protective exudate that eventually coats the twigs, furnishing stick lac. This is collected and purified to the shellac of commerce by rolling, crushing, separating, washing, and bleaching. See Chap. 34.

Overshadowing these natural products are the more recently introduced synthetic resins (Chap. 34). The ranking of synthetic resins by use in industrial finishes is: alkyds, acrylics, epoxies, nitrocellulose, phenolics, urethanes, and the newer promising but expensive types now used in lesser amounts—siliconized alkyds, polyesters and acrylics, fluoropolymers, and polyimides. Phenolic resins (phenol-formaldehyde) were the first of these to be supplied and are still in wide use since they are very resistant to water and many chemicals. In order to make these materials soluble in the oils and solvents in common use in the varnish industry, it is necessary to modify them. This may be done either by fluxing them with softer materials such as ester gum or by controlling the polymerization reaction by choosing a para-substituted phenol, thus stopping the reaction before a final insoluble, infusible product is obtained.

Alkyd resins are formed by condensing dicarboxylic acids with polyhydric alcohols and are modified with fatty acids to gain solubility. As a constituent of varnishes or enamels, they have the distinctive properties of beauty and flexibility which are retained upon prolonged exposure to weather. With their introduction, the surface-coating industry became synthetic minded. The properties of the alkyd formulation may be modified by the use of different fatty acids or oils of both drying and nondrying types, by the use of pentaerythritol for glycerin, by the use of maleic or other dibasic anhydrides for all or part of the phthalic anhydride, and by modifying with other resins (phenolics, rosin, and the like). As such, they find extremely diversified applications in various coating formulations. They have largely replaced varnishes of the oleoresinous type.

Ester gum, the product of the esterification of the abietic acid or rosin with glycerin, is another important raw material for making varnish. In addition to the coumarone-indene types, urea-formaldehyde types, and melamine-formaldehyde resins, some of the newer resins include acrylics, silicones, and vinyls.

Epoxy resins are now widely used for protective and chemical-resistant coatings but fail to meet the mass production requirements of the furniture industry. Quick-drying urethane

[12]Payne, *Organic Coating Technology*, vol. 1, Wiley, New York, 1955, p. 138.

coatings have recently moved from the specialty finish field into broader markets. Original urethane lacquers had two drawbacks, an isocyanate vapor hazard and a two-pot system; now they may be applied from the can. The new finishes fall into two classes: (1) Isocyanate nonreactive oil-modified urethanes make use of toluene diisocyanate (TDI) in combination with polyols such as glycerin, methyl glucoside, linseed, and soybean oil. Major uses are for exterior wood, such as for siding, shingles, boats, and also for interior floors and furniture. (2) Isocyanate reactive types are made by reacting excess TDI or an aliphatic or cycloaliphatic isocyanate with a hydroxyl-bearing substance to form a prepolymer, which then reacts further with the hydroxyl groups of the polyol (first category) or with moisture (second category) to form the film. The use of aliphatic isocyanates has produced coatings of much greater durability. Synthetic resins have numerous advantages over naturally occurring types, such as superior resistance on exposure to weather and chemicals, the ability to be baked more rapidly at higher temperatures, and higher solid content than nitrocellulose lacquers, making a one-spray operation possible.

LACQUERS

Lacquer is a loosely used term. It refers to a coating composition based on a synthetic, thermoplastic, film-forming material dissolved in organic solvents, which dries primarily by solvent evaporation.[13] Confusion between lacquers and enamels remains in the public mind, which is not surprising in view of the standard definition of an enamel as a paint characterized by the ability to form an especially smooth film. Clear lacquers, upon addition of pigment, become lacquer enamels, or simply pigmented lacquers. Lacquer use is currently limited to coating furniture. When used to coat automobiles, enamels are habitually referred to as lacquers.

Surface coatings packed in pressurized cans (aerosols) are usually lacquers (clear, colored, or metallic), but vinyl coatings resistant to abrasion, sunlight, and moisture; epoxies, and stainless-steel flakes in vinyl or expoxy designed to prevent corrosion of machinery are available.

INDUSTRIAL COATINGS

Alkyd resins are used extensively in industrial coatings. They are widely compatible with oils and other resins, but their durability and resistance to water, sunlight, and chemicals is inferior to that of phenolics.

Phenolics are used to resist alcohols and food acids, particularly in cans and containers, but their use in varnish has lost out to urethanes and other film formers.

Acrylics, available as thermoplastic and thermosetting types (with mixtures compatible), represent the current optimum combination of price, durability, flexibility, and appearance. They are used in automotive topcoats.[14]

Epoxies are used in plants where chemical resistance is essential. They require a curing agent and are expensive. They are used on appliances, as linings, and for prime coats.

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[13]ASTM Standards, vol. 28, 1982.

[14]Zimmt, Coatings from Acrylic Polymers, *CHEMTECH* **11** (11) 681 (1981); Curing Paints at Room Temperatures, *Chem. Week* **132** (2) 52 (1983).

The urethanes are strongly adherent to metal and resist both chemical attack and abrasion. Their clarity and resistance to weather make them useful for severe industrial service.

Fluoropolymers represent the current maximum in weather resistance. The slick surface and good wear resistance cause them to be used as coatings for snow shovels, saws, aircraft, and chute liners.

Polyimide resins are used to coat special pans and other material that must resist temperatures of 275°C continuously or 450°C maximum briefly.

APPLICATION. Traditional application with a brush is increasingly proving too time-consuming. Dip tanks provide cheap application, but coating is uneven and holidays in the coatings are common. Conventional spray equipment is cheap to own and maintain, but gives uniform results only in the hands of skilled operators and frequently results in highly variable film thickness. Spraying is increasingly coming under fire because of its pollution of the air with both volatile solvents and finely divided solids. Electrostatic spraying, in which the paint droplets are made to carry a charge of one polarity while the object being painted is oppositely charged, sharply reduces waste and gives a uniform coat. Its use is limited to metal objects in spray booths. Coil coating of sheets by passing them through baths, sometimes followed by leveling rollers, is efficient in the use of fluids, but edges are hard to coat properly. Electrodeposition[15] may be used with aqueous dispersions of alkyds, polyesters, epoxies, and acrylics solubilized with alkalies such as diethylamine, ammonium hydroxide, and potassium hydroxide. Great coating uniformity is achieved by anodic or cathodic deposition using voltages of 300 to 450 V. The flow of current automatically stops when a coating of 25 to 40 μm has formed because of the insulating properties of resins. The coated part requires about 30 min at 175°C to produce a cross-linked thermoset polymer film. In anodic coating, iron is dissolved from the metal and thus corrosion starts before the steel is coated. Current practice favors cathodic coating where the metal ions are held back and the positive resin ions deposit on the steel.

Fluidized-bed coating and electrostatic spray coating are used to coat metals with powders which are then fused.[16] These techniques are used with epoxies, vinyls, nylons 11 and 12, polyethylene, polypropylene, chlorinated polyethers, melamines, and, no doubt, several other compounds. Air pollution is avoided, and coating quality is excellent, but color problems and wastage cause trouble.

Electron-beam (EB) radiation curing has been tested and shows promise. EB curing works very fast and requires no heat. Prepolymers are cured by using an accelerator's beam. Coatings of baked quality can be produced over heat-sensitive materials such as wood or plastic.

Autodeposition is a new metal finishing technology which activates chemically rather than electrically. It uses aqueous dispersions of polymer, pigment, and metal activators and is operated at room temperature. A high coating efficiency is claimed for this method, which simultaneously pretreats and coats the metal.[17]

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[15]Roobol, Painting with Electricity, *CHEMTECH* 12 (8) 493 (1982); Springer, Strosberg, and Anderson, Conductivity Control of Cathodic Electrocoating, *J. Coat. Technol.* 54 (689) 57 (1981).

[16]*Hercules Chem.*, December 1972, p. 1; Conte, Painting with Polymer Powders, *CHEMTECH* 4 (2) 99 (1974); Powder Paint Gets a Ride on a Pinto, *Chem. Week* 116 (2) 41 (1975).

[17]Hall, Autodeposition: A Survey of a New Water-Borned Coating Technology, *J. Coat. Technol.* 52 (663) 72 (1980).

Precoating of metals, such as steel and aluminum strips, before fabrication is now widely practiced in the coating field. Roller coaters are unsurpassed in speed and surface quality for coating either one or both sides of continuous strip stock. Resins used are shown in Table 8.5.

MARINE ANTIFOULING COATINGS[18]

The problem of preventing fouling of surfaces exposed to the marine environment has been with human beings since recorded history. Originally tar and pitch coatings and copper sheathing were used; later lead sheathing came into use. With the advent of steel ships, metallic sheathing had to be abandoned because of galvanic corrosion. At present, the use of copper oxide in either an insoluble vinyl resin binder or a soluble vinyl resin-rosin binder is common. These work by slowly releasing the toxic copper oxide, but the toxic action slowly decays because of the presence of hydrogen sulfide in polluted waters which results in inactive copper sulfide being formed. The newest and most promising approach is the use of organotin compounds, either alone or combined with copper oxide. Paints containing tributyl tin oxide and/or tributyl tin fluoride are being used. Tests of coatings of organotin compounds chemically linked to a film-forming polymer are showing increased antifouling activity. These coatings are very slightly water soluble so that a fresh film of biocide is constantly being exposed.

PRINTING INKS AND INDUSTRIAL POLISHES

Printing inks consist of a fine dispersion of pigments or dyes in a vehicle which may be a drying oil with or without natural or synthetic resins and added driers or thinners. Drying oils or petroleum oils and resins are employed, although the newer synthetic resin systems are finding great favor because they are quick-drying and their working properties are excellent.

[18]Gitlitz, Recent Developments in Marine Antifouling Coatings, *J. Coat. Technol.* 53 (678) 46 (1981); Coatings Make for Smooth Sailing, *Chem. Week* 125 (4) 42 (1979).

Table 8.5 Industrial Coatings

Industrial Finishes Market	Resins in Industrial Finishes
Appliances	Acrylics
Automotive, marine, and aircraft	Alkyds, acrylics
Containers and closures	Epoxies
Industrial and farm equipment	Fluoropolymers
Maintenance	Nitrocellulose
Metal furniture	Phenolics
Paper and flexible packaging	Polyesters
Sheet, strip, and coil coating	Polyimides
Wood furniture	Polyurethanes
	Polyvinyls
	Siliconized polymers
	Ureas and melamines

Printing inks have a large variety of compositions and wide variations in properties.[19] This is because of the great number of different printing processes and types of papers employed. The expensive new magnetic inks, developed for use in a number of electronic machines, are the keys to one type of data processing system. Inks formulated with luminescent pigments achieve a superbright effect; dyes are melted into the resin and baked and, when hard, the material is easily powdered. Rhodamines, auramines, and thioflavins are the principal dyes used in heat-set inks.

Polymer polishes, which have captured 85 percent of the total polish market, have become increasingly popular both in industrial applications and in the large household field. Present-day polishes of the self-drying water-emulsion type had their start in the leather industry in 1926 and since then have undergone numerous improvements.

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[19]Miron, Printing with Polymers, *CHEMTECH* 9 (12): 746 (1979). George, The Challenges of the Eighties in Coatings and Graphic Arts, *J. Coat. Technol.* 53 (674) 1981.

PART 2

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Chapter 1

Nuclear Industries

In the early years of this century, Wilhelm Ostwald, a famed physical chemist, advanced the hypothesis that energy, not mass, is the fundamental basis of matter. Despite this view, colleges continued to teach conservation of mass along with energy for several decades. Becquerel discovered radioactivity in 1898, and the existence of isotopes was shown around 1900. These findings pointed the way to nuclear processes. Reactions involving atomic nuclei showed that matter could be transformed into energy.[1] Fission of the atom was demonstrated by Fermi, followed by Meitner and Frisch. Fission of uranium into two nearly equal fragments yields a tremendous amount of energy that appears as heat accompanied by the emission of neutrons and gamma rays with the simultaneous disappearance of a corresponding amount of mass in accordance with the well-known Einstein equation $e = mc^2$. These discoveries were put to practical use in the form of a sustained chain reaction under the direction of Fermi at the University of Chicago on December 2, 1942, using a nuclear reactor, or pile, of graphite and uranium with a critical mass of a few tons of extremely pure uranium and uranium dioxide. The extremely pure uranium dioxide used and all the early pure uranium metal were manufactured using an ether extraction purification of uranium nitrate hexahydrate. Such purification of inorganic materials with organic solvents represented a new and extremely effective approach to the manufacture of high-purity inorganic salts.

Controlled fission generates heat which can be used to produce steam to drive prime movers, thus generating electricity. The radiation produced during fission can also be used for the synthesis of various isotopes of elements.

Except for incoming solar energy, all world energy sources are finite and exhaustible, and they are being exhausted. Coal, shale oil, petroleum, lignite, and peat are solar derived, have been stored up over millennia, and are being rapidly used up. Probably oils and coal should be conserved as raw materials for use in the process industries; certainly their use as a fuel is not appropriate nor is it in the best long-term interests of humankind. The broad distribution of uranium (and thorium) suitable for centuries of generation of heat and electricity[2] is a fortunate circumstance and extends the prospects for comfortable energy-consuming existence well beyond the time when cheap oil and gas have been exhausted. Figure 21.1 shows the uranium cycle.

There is an energy shortage in many localities of the world at present because of the difficulty in obtaining sufficient supplies of fuel, primarily coal, oil, and gas. Temporarily, there exists a surplus of uranium fuel. Energy obtained through nuclear fission can greatly reduce the energy shortage. Over 10 percent of the total power used in the United States is currently nuclear-generated. In some parts of the country (e.g., Chicago), around 90 percent of the electricity used is from nuclear units.

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[1]Glasstone, *Sourcebook on Atomic Energy*, 3d ed., Van Nostrand, New York, 1967.

[2]ECT, 3d ed., vol. 16, 1981, p. 138.

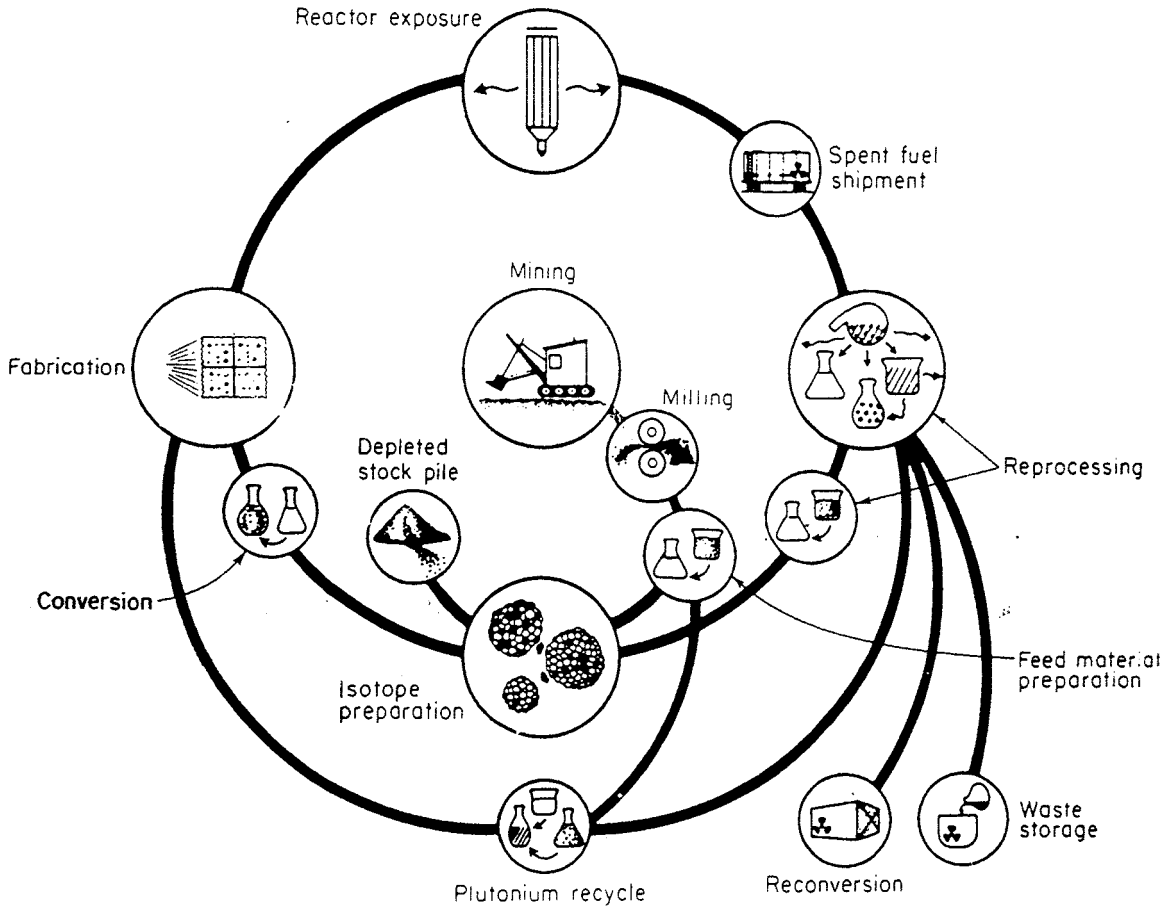

Fig. 21.1. Fuel cycle: from uranium mine through many steps, including plutonium reactor to recycle reconversion and wastes. *(R. H. Graham, World Uranium Reserves and Nuclear Power.)*

In August 1982,[3] 274 nuclear units producing 155 GW_e (GW_e = electrical GW) were operating in the world. Of these, 58 percent were pressurized water reactors (PWR), 24 percent boiling water reactors (BWR), 13 percent graphite-moderated, 4.2 percent heavy water–moderated, and 0.6 percent were fast breeder reactors (FBR). Two hundred thirty more units designed to produce 208 GW_e were under construction, and 151 more units to produce 150 GW_e were planned. The later units show increases in the percentage of PWR and FBR with reductions in the other types.

The accident at the Three Mile Island generating plant near Harrisburg, Penn. on March 28, 1979, coupled with a decline in electrical power demand (caused by higher rates and declining business activity) has caused the cancellation or delay of a number of planned nuclear and fossil-fueled plants. The accident also showed the workability of the "defense in depth" safety concept used in all reactors. Although several of the safeguards failed and human response to problems was most erratic, the accident was stopped at a point far short of catastrophe and no one was exposed to significant radiation. Public health hazard was trivial with the statistical probability that radioactive gases released to the atmosphere will cause no more than 0.7 deaths in the next 30 years. Despite this, emotional response to the accident has hampered the expansion of the whole nuclear program.

As each new type of energy has been put at our service, it has encountered public resistance. Coal, steam power, and electrical energy use, for example, have been resisted by pop-

[3]Power Reactors 1982, a Directory of the World's Power Reactors, *Nucl. Eng. Int.* 27 (330) 2–76, (1982).

ılist groups claiming "unnaturalness." Nuclear power is encountering such resistance now, nd undoubtedly fusion will also be resisted when it develops. Major difficulties have also risen because of delays in construction combined with high interest rates. Capital costs have kyrocketed, due in part to constantly altered regulations which make for still greater construction delays. Construction workers' productivity has been low. No other chemical process ndustry endures such pervasive government control.

The dangers of nuclear power use, as seen by some persons, arise to some extent from the lestruction observed from the use of the atomic bomb. Such high-power explosions would ıot occur in the very unlikely case of a major nuclear reactor accident. Inadvertent criticality elf-limits at 316 to 31,600 kJ and would not cause a bomb-type explosion.[4]

VUCLEAR REACTIONS

The first spontaneously decaying substances discovered were radium and polonium isolated ɔy the Curies in a marvelous scientific achievement. Nuclear reactor–produced isotopes now ·eplace these substances for industrial and medicinal uses and are far cheaper and safer.[5]

URANIUM AND THORIUM FISSION

Under appropriate conditions, neutrons react with uranium and thorium to produce new isotopes, some stable, others having extremely short half-lives. A ^{235}U atom absorbs a thermal (i.e., relatively slow) neutron, then fissions (splits) into fragments of approximately one-half the original atomic weight, gives up neutrons, and a substantial amount of heat energy.

$$^{235}U + \text{neutron} \rightarrow \text{fission products} + \text{energy} + 2.43 \text{ neutrons.}$$

Figure 21.2 shows the range of products formed by the bombardment of ^{235}U with slow and fast neutrons. This is the well-known "camel's hump" curve.

Neutrons released by fission are at high energy levels (fast neutrons) and can react in fast reactors, but most reactors require that they be slowed down to thermal speeds before they can be captured by (i.e., react with) ^{235}U. Slowing down is done by repeated elastic collisions with the so-called moderators, substances such as carbon, H_2O, or D_2O which absorb few neutrons but permit elastic collisions. Of the 2.43 neutrons released, one is needed to continue the chain reaction, and the others may bring about other nuclear reactions or be lost through leakage or capture by elements in the reactor.

Naturally occurring uranium contains only 0.71% ^{235}U, the remainder being ^{238}U. To sustain the chain reaction and obtain usable energy, the ^{235}U content is increased by isotope separation and concentration.

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[4]ECT, op. cit.

[5]Benedict, Pigford, and Levi, *Nuclear Chemical Engineering*, 2nd ed., McGraw-Hill, New York, 1982.

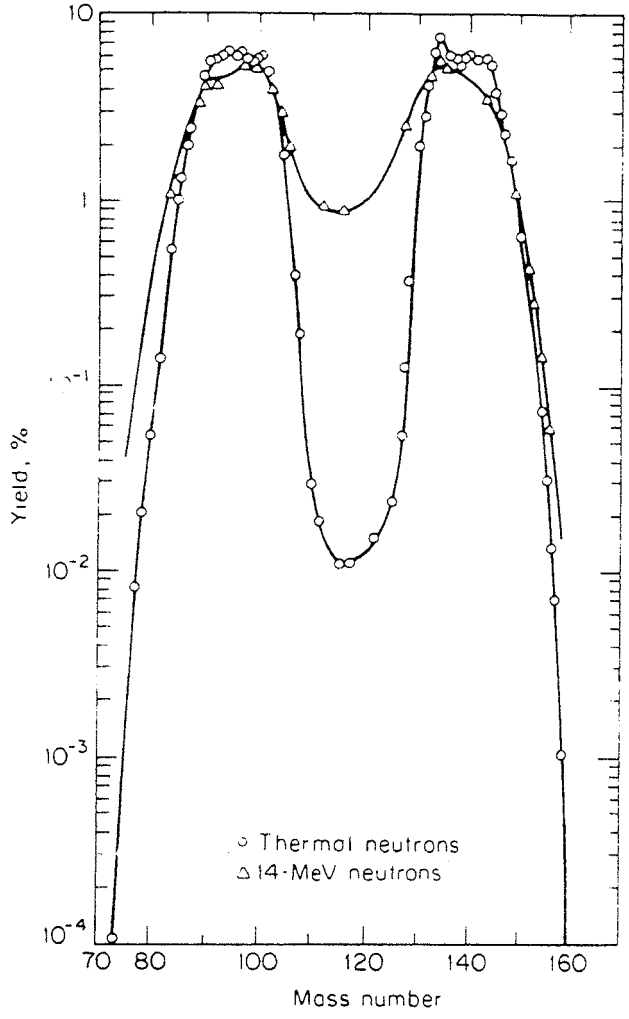

Fig. 21.2. ^{235}U fission product yield against mass number. (*ANL 5800.*)

Unmoderated natural uranium cannot sustain a chain reaction. Enrichment with ^{235}U reduces reactor size and increases the period between fuel replacements. The common isotopes of uranium and thorium, ^{238}U and ^{232}Th, do not split (fission) on absorbing a neutron, but do form other elements that undergo rapid, spontaneous decay to yield isotopes that are fissionable, so they are usable for power production.

The reactions are:

$$^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U \xrightarrow[23\ \text{min}]{\beta,\gamma} {}^{239}_{93}Np \xrightarrow[2.3\ \text{days}]{\beta,\gamma} {}^{239}_{94}Pu\ (\text{fissile})$$

$$^{232}_{90}Th + {}^{1}_{0}n \longrightarrow {}^{233}_{90}Th \xrightarrow[23\ \text{min}]{\beta,\gamma} {}^{233}_{91}Pa \xrightarrow[27\ \text{days}]{\beta} {}^{233}_{92}Th\ (\text{fissile})$$

Isotopes that are not fissile but are convertible to fissile materials are called fertile materials. The synthesis of such elements and other heavier ones, the transuranic elements, on a large scale is an important scientific development. ^{239}Pu has a long half-life (24,000 years) and is quite important because it has a high cross section (ability to absorb) for fast neutrons and a low critical mass for fast fission, desirable properties for military applications. The Savannah River, S.C. plant is the major U.S. manufacturing facility for weapons-grade plutonium. Fuel-grade plutonium is produced as a by-product of water-moderated power reactors.

URANIUM AS AN ENERGY SOURCE

The diminishing availability of reasonably priced fossil fuels has led to conservation practices which have decreased the energy demand. Conservation is certainly desirable. The decreased energy demand and the emotional public outcry against reactors following the Three Mile accident have reduced the demand for uranium as fuel and created a temporary surplus. Capital costs for electrical energy made in nuclear-fueled plants are greater than for traditional fuels, but uranium is the lowest cost fuel available at present and its price has risen at a lower rate than those of other fuels during the last 15 years as shown in Table 21.1. At the present, electricity generated by nuclear plants and that from fossil fuels are virtually identical in total cost.[6] The greater safety and cleanliness of nuclear units should ultimately make them the more attractive choice.

The current price of uranium ($70 to $77 per kilogram in 1982) is depressed by low demand, but with present technology, uranium at $110 per kilogram is cheaper than residual oil at $250 per metric ton. A $1 per kilogram increase in the price of U_3O_8 is equivalent to 10 cents per metric ton increase for coal or 17 cents per metric ton increase for oil. These figures show that as a base load fuel, uranium is clearly cheaper than oil at the present time. Of course, fuel is only one of the major costs involved in power generation. Waste disposal and decommisioning costs have become major considerations. Solid waste disposal costs for coal have been estimated by the General Accounting Office of the U.S. government (in 1980) as costing roughly three times more than that for nuclear waste (coal between 1.0 and 1.2 mills/MJ, nuclear 0.22 to 0.36 mills/MJ). The CO_2 and SO_2 in the gaseous fossil fuel discharge are also objectionable and may ultimately require limitation.

There exists the virtual certainty that demand for uranium will continue and increase. The U.S. known sources of available energy show uranium as the major reserve. See Table 21.2.

Uranium in the United States is found in sandstones of the Colorado plateau, basins in Wyoming, and the gulf coast plains of Texas. It is also present in phosphate rock in Florida and the western states and can be recovered as a by-product of processing for the manufacture of phosphatic fertilizers. By-product concentrations as low as 50 to 130 ppm are workable. Rich ores are present in Canada and Africa. States producing uranium are (in order of production) New Mexico, Wyoming, Texas, Colorado, Florida, Utah, and Washington.

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[6]Crowley and Griffith, U.S. Construction Cost Rise Threatens Nuclear Option, *Nucl. Eng. Int.* **27** (238) 25 (1982).

Table 21.1 Cost of Fuel for Electricity Generation, 1965 to 1980 (Fuel cost data in cents per GJ = 10^9 J)

Fuel	1965	1970	1975	1980
Bituminous coal	19.0	26.4	91.8	152.8
Subbituminous coal	11.6	13.7	52.4	120.2
Residual oil	36.9	52.7	212.4	451.3
Natural gas	26.4	28.5	79.5	224.6
Nuclear fuel	21.1	23.2	30.6	39.6

SOURCE: C. M. Valorie, *Power Plant Fuels and Their Effects on the Cost of Electricity*, United Engineers and Constructors.

Table 21.2 U.S. Uranium Energy Available Exceeds Other Known Sources

Resource	Available Energy, EJ (10^{18} J)
Uranium	137,500
Coal and lignite	12,700
Oil shale	6,120
Petroleum and natural gas liquids	1,160
Natural gas	1,090

SOURCE: U.S. Department of Energy.

NUCLEAR FUELS

SOURCES AND RESERVES. In the early years of the nuclear industry, South African ores of various types and Canadian pitchblende were the major sources. In later years, larger supplies of uranium ore came from domestic sources as shown in Table 21.3.

Uranium is more abundant in the earth's crust than mercury and is present in about the same amount as tin and molybdenum. It is widely distributed.

Thorium, while less widely used than uranium, is a suitable nuclear fuel. A commercial thorium-fueled reactor operates at St. Vrain, Colo. and an experimental light water–moderated thorium-fueled breeder reactor is at Shippingport, Penn.

Thorium exists with only one natural isotope, ^{232}Th, and is not very rare. Most of it is obtained as a by-product of the processing of monazite, a complex phosphate, for the extraction of rare earths. Major deposits are found in India, Brazil, Union of South Africa, Australia, Malaysia, and the United States. Reserves are substantial and hardly utilized yet.

MINING AND MILLING ORE.[7] Figure 21.3 shows the main steps from ore to usable nuclear materials. The purification utilizes an organic solvent extraction, a difficult isotope separation process, and finally a unique process—the synthesis of an element, plutonium.

The steps are:

1. Mining of the ore. Mined U.S. ores carry only a low concentration (around 0.2% U_3O_8) of uranium.

[7]Merritt, *The Extractive Metallurgy of Uranium*, Colorado School of Mines, Golden, Colo., 1971.

Table 21.3 U.S. Uranium Statistics: 1970 to 1980 (in thousands of metric tons of U_3O_8)

	1970	1975	1978	1979	1980
Recoverable U_3O_8	11.6	10.9	17.1	14.3	18.2
Production, concentrate	11.7	10.5	16.8	17.0	19.9
Imports, concentrate*	—	0.6	2.4	1.5	1.6
Free world production	22.0	22.5	40.1	44.9	51.5

*Mainly for enrichment prior to 1977.

SOURCE: U.S. Department of Energy, *Statistical Data of the Uranium Industry*, 1981 and 1980, annual report to Congress, vol. 11.

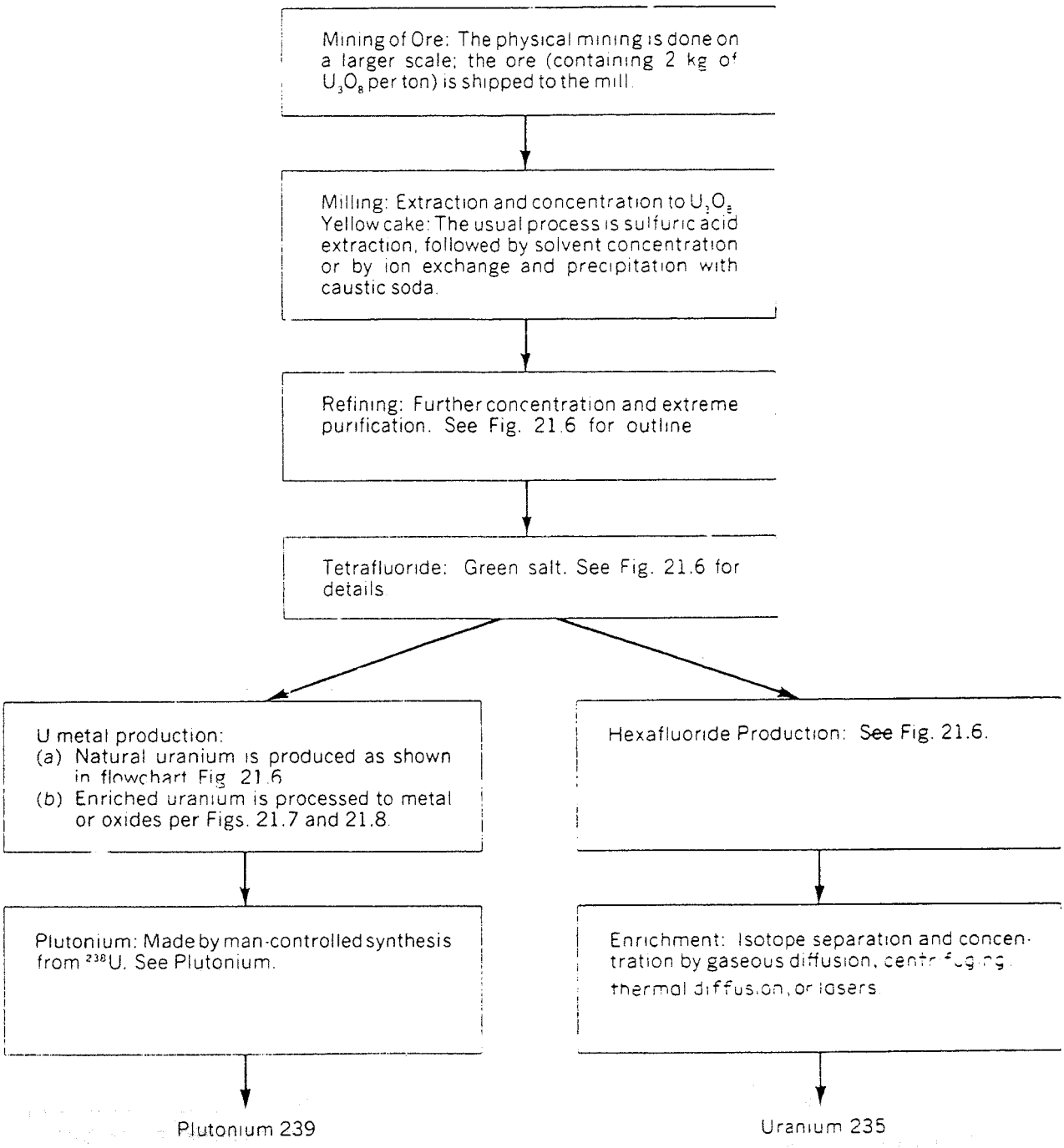


Fig. 21.3. General outline of chemical flowchart from ore to usable nuclear material

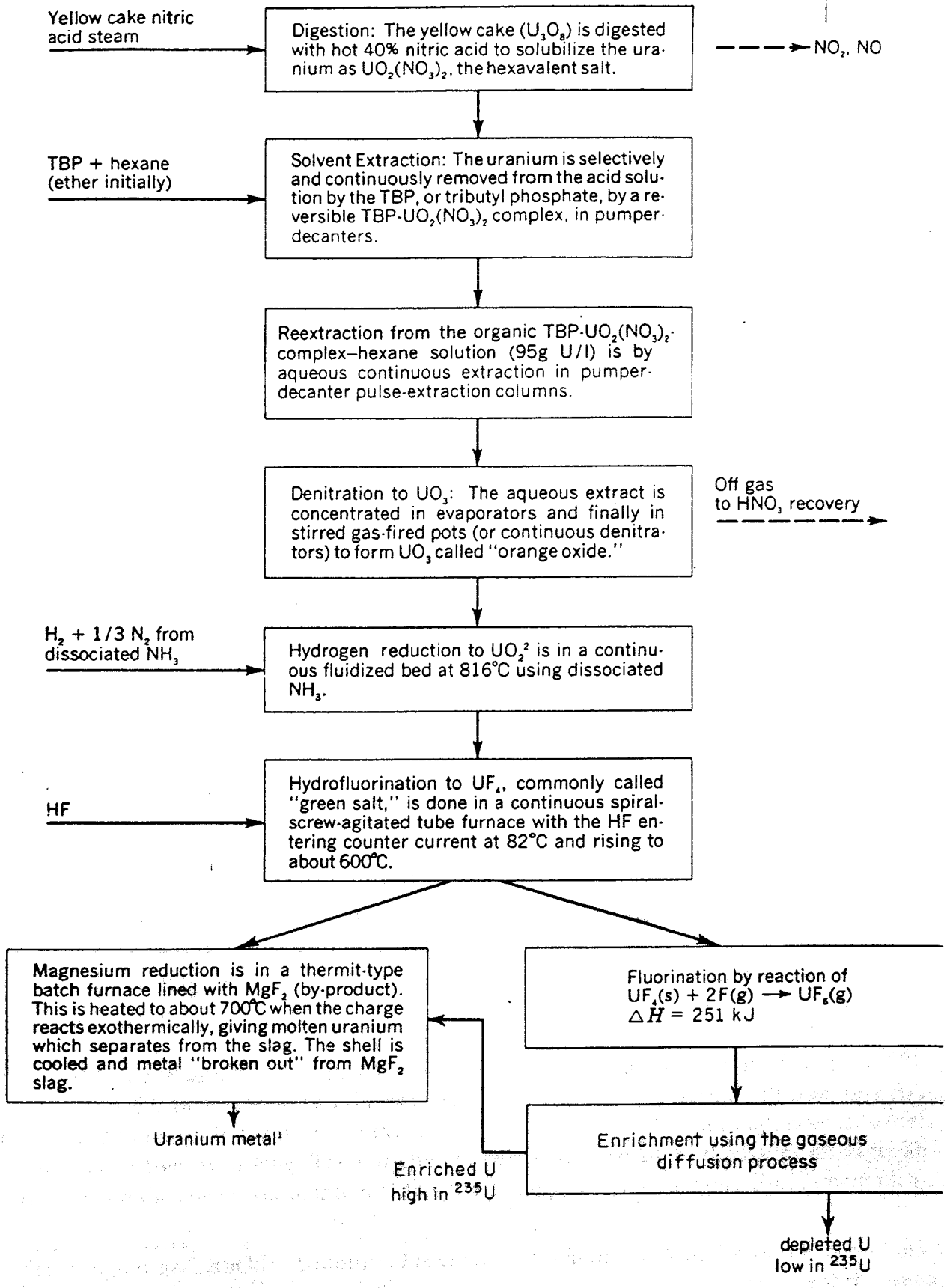
2. Milling and extraction to produce impure U_3O_8 or yellow cake. Ores are usually leached with sulfuric acid, then the weak leach solutions are concentrated by ion-exchange or solvent extraction, and finally yellow cake is precipitated with caustic soda. The tailings contain a small amount of radioactive material.

3. Refining and purification to produce extremely pure uranium by procedures outlined in Fig. 21.4. $UO_2(NO_3)_2 \cdot 6H_2O$, UO_2, UO_3, UF_4, and UF_6 (and sometimes metallic U) are all involved.

4. Isotope enrichment in ^{235}U, usually by separating $^{235}UF_6$ from mixed isomers of UF_6 using gas diffusion.

5. Conversion of UF_6 to UO_2 or U.

6. Nuclear fuel fabrication, generally as UO_2, UC, or U.



[1] At one time the uranium was remelted for purification but now a direct ingot, or "dingot", reduction is practiced giving a 1550 kg "dingot".

Fig. 21.4. Refining of uranium: feed-material-plant flowchart.

7. Mechanical forming, involving pressing, sintering, and grinding to precise size.
8. Element fabrication. Cladding, sealing, pressuring, and assembling into units.
9. Reaction in a nuclear reactor to produce power and/or plutonium.

REFINING AND PURIFICATION.[8] Conversion of crude yellow cake or uranium metal to material pure enough for reactor use, i.e., free of other elements, particularly neutron absorbers, is required. Boron and cadmium are particularly troublesome and must be below 1 ppm. The process for accomplishing this was a closely guarded secret until the end of World War II. Figure 21.4 shows the essential steps of the process as operated at Savannah River, S.C. or Hanford, Wash. Uranyl nitrate hexahydrate is quite soluble in ethyl ether, tributyl phosphate-kerosene, or TBP-hexane solutions. Contaminants show virtually no solubility. These extractions make a very clean separation of uranium from other inorganics possible, yielding high purities with few steps. This organic extraction procedure is also useful in treating irradiated fuel elements from reactors to separate uranium and plutonium.

The reactions involved are as follows.

DISSOLVING

$$U_3O_8 + 8HNO_3(aq) \rightarrow 2UO_2(NO_3)_2(aq) + 2NO_2 + 4H_2O \qquad \Delta H = -173 \text{ kJ}$$

or

$$UO_2 + 4HNO_3(aq) \rightarrow UO_2(NO_3)_2(aq) + 2NO_2 + 2H_2O$$

or

$$U + 5.5HNO_3(aq) \rightarrow UO_2(NO_3)_2(aq) + 2.25NO_2 + 1.25NO + 2.75H_2O$$

Solvent extraction then yields very pure uranium nitrate hexahydrate, which is converted to volatile UF_6 by the following reactions:

$$UO_2(NO_3)_2 \cdot 6H_2O \xrightarrow{\text{heat}} UO_3 + 2NO_2 + \tfrac{1}{2}O_2 + 6H_2O(g) \qquad \Delta H = +563 \text{ kJ}$$

$$UO_3(s) + H_2 \rightarrow UO_2(s) + H_2O(g) \qquad \Delta H = -106 \text{ kJ}$$

$$UO_2(s) + 4HF(g) \rightarrow UF_4(s) + 2H_2O(g) \qquad \Delta H = -181 \text{ kJ}$$

$$UF_4 + 2Mg \rightarrow U + 2MgF_2 \qquad \Delta H = -350 \text{ kJ}$$

$$UF_4(s) + F_2(g) \rightarrow UF_6(g) \qquad \Delta H = -251 \text{ kJ}$$

ISOTOPE ENRICHMENT.[9] Two major processes are used today to separate ^{235}U from ^{238}U: The gaseous diffusion process and the gas centrifuge process. The gaseous diffusion process is based on differences in the diffusion rate between $^{235}UF_6$ and $^{238}UF_6$ through porous barriers several mean free paths long. The enrichment per stage is small, so thousands of stages are required and the power consumption of the interstage pumps is enormous. Enrichment plants

[8]Harrington and Ruehle, *Uranium Production Technology*, Van Nostrand, New York, 1959.

[9]Voigt, "Status and Plans of the DOE Uranium Enrichment Program," AIChE Meeting, March 1982.

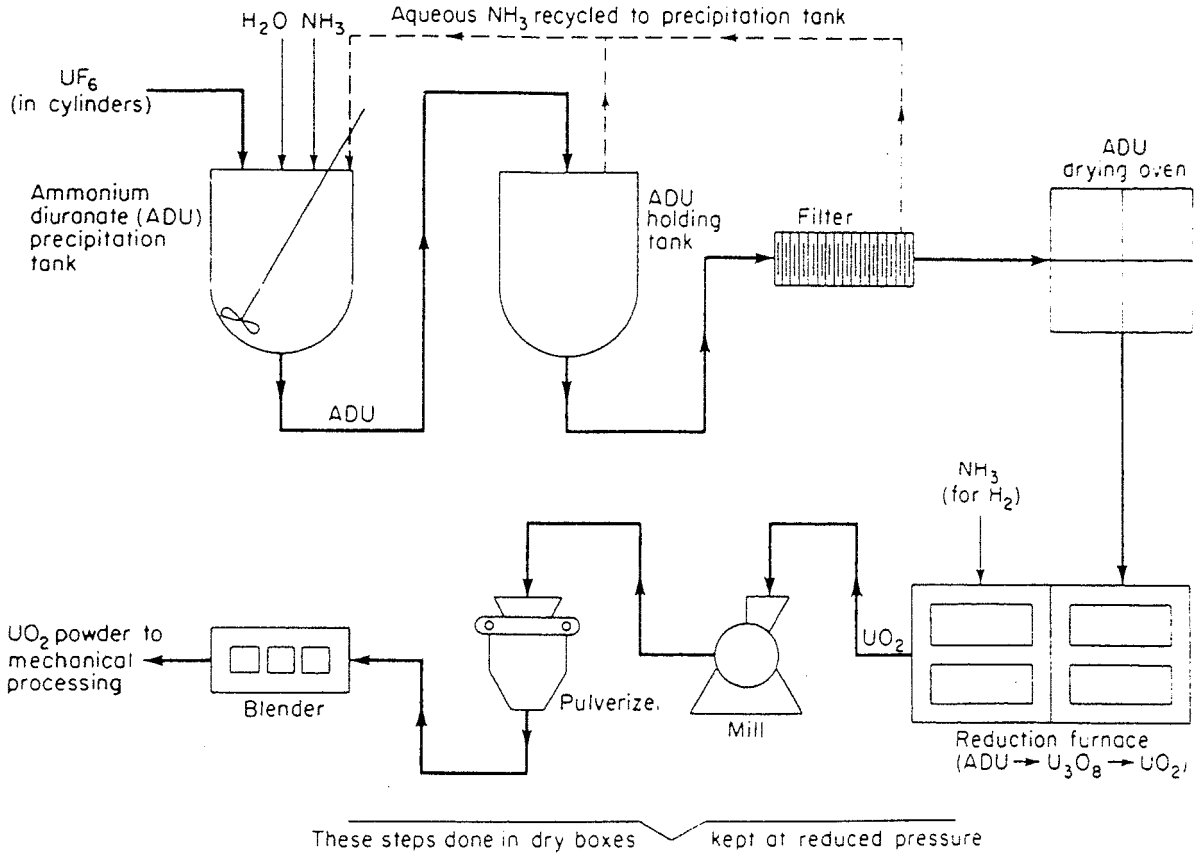


Fig. 21.5. UF_6 to UO_2 by the ammonium diuranate process. *(United Nuclear Corp. and Industrial and Engineering Chemistry.)*

in the United States consumed 4.1 percent of the country's entire electrical power output in 1970. Maximum enrichment is 94% ^{235}U, with a waste containing about 0.3% ^{235}U.

The gas centrifuge process depends on centrifugal force for the separation. Capital expense is greater than for a diffusion plant, but the energy requirement is only ⅒th as great. The United States is building a gas centrifuge plant in Portsmouth, Ohio to start operation in 1985 and which will have a capacity of 38 percent of that of the present two gas diffusion plants.

Voigt[9a] has estimated the 1982 relative costs as $180 per SWU (separative work units—units of capacity) for the diffusion process with a corresponding cost for the centrifuge process of $70 to 80 per SWU with the probability of a drop of 20 to 50 percent in the near future.

Other exotic processes continue to be suggested and/or tested. Three such advanced isotope separation (AIS) processes are currently being developed in the United States by the Department of Energy (DOE). These are known as the plasma separation process (PSP), the atomic vapor laser isotope separation (AVLIS) process, and the molecular laser isotope separation (MLIS) process. The cost of a SWU by these processes has been estimated at $30 to $40, but much remains to be done and none is likely to be practical before 1990. As nuclear power becomes increasingly important, the expensive separation process will require much expansion, and it is hoped that new processes can reduce costs dramatically.

CONVERSION. UF_6 can be converted to UO_2 through the process shown in Fig. 21.5. A high degree of protection against even minor contamination is essential if the necessary purity is to be obtained.

[9a]Voigt, op. cit.

Nuclear Fuels Selection

The three fissionable isotopes, ^{233}U, ^{235}U, and ^{239}Pu, have a higher probability of fission than capture when absorbing a neutron. These are the only common materials which can sustain a nuclear fission reaction, and therefore they are the nuclear fuels. Of these isotopes, only ^{235}U occurs in nature. The other two are reactor-synthesized and extend the amount of fissionable material far beyond that which occurs naturally. Fuels for reactor use must have suitable physical as well as nuclear properties. Solids are usually preferred, so UO_2, ThO_2, PuO_2, and mixtures in the form of sintered, high-density pellets are commonly used. Other combinations that have been used are: uranium-aluminum alloys, uranium sulfate solutions, plutonium-aluminum alloys, U_3Si, UC_x, and Pu metal alloys and cermets. UO_2 enriched to varying percentages of ^{235}U is widely preferred because of its high melting point (2176°C), good thermal conductivity, high density, and resistance to the effects of radiation. Fuel is usually prepared from UF_6 enriched to the desired percentage. Figures 21.5 and 21.6 illustrate the steps required.

MECHANICAL FORMING AND ELEMENT FABRICATION. To form fabricated fuel elements, fuels are pressed, sintered; ground to exact size; inserted in a sheath of stainless steel, zirconium, or one of the zircalloys; pressurized with helium; carefully welded shut; then assembled into convenient sized groups for handling. Some work must be done by remote control or in glove boxes. Preparation is tedious and exacting, and quality control is of the utmost importance.

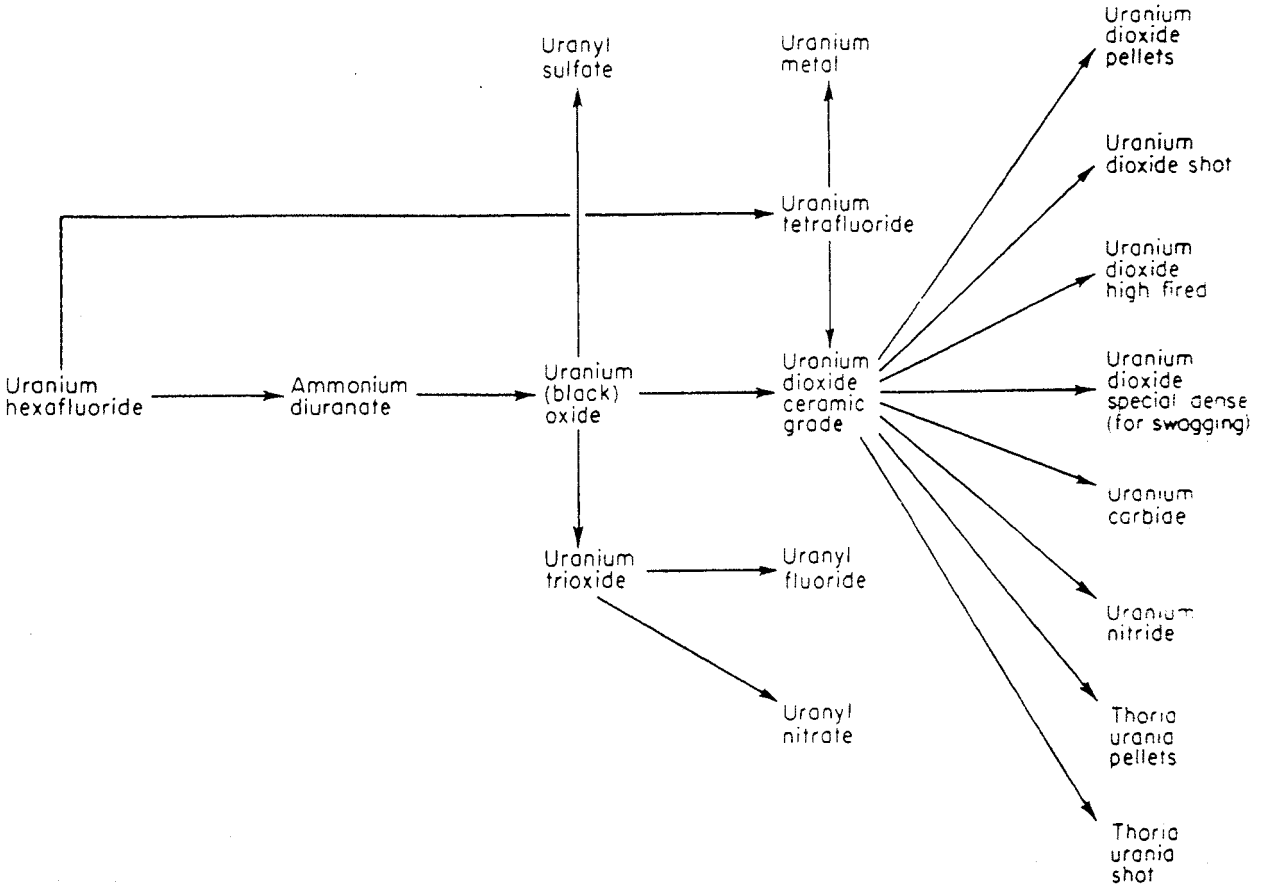


Fig. 21.6. UO_2 production flowchart. *(United Nuclear Corp.)*

NUCLEAR REACTORS

Nuclear reactors have been defined[10] as devices "containing fissionable material in sufficient quantity and so arranged as to be capable of maintaining a controlled, self-sustaining nuclear fission chain (critical) reaction."

There are three major types of reactors now operating: burners, breeders, and converters. In addition, many other classifications and subgroups are possible.[11]

BURNERS. Burners commonly use uranium enriched in ^{235}U and some type of moderator to produce heat and slow down the neutrons to maintain the chain reaction. The fuel gradually becomes depleted. See Figs. 21.7 and 21.8.

Figure 21.7 describes the reactor vessel and core. The core consists of approximately 200 nuclear fuel assemblies which are grouped together to make up the core of the reactor. Interspersed among the fuel assemblies are movable control rods, which are made of a material that readily absorbs neutrons. When the control rods are inserted into the core, the nuclear chain reaction in the fuel assemblies is slowed down, and this reduces the amount of heat produced in the core. Withdrawal of the rods speeds up the chain reaction and more heat is produced. The entire reactor core, which contains fuel assemblies and control rods, is enclosed in a heavy stainless-steel vessel. As an added safety feature, the entire reactor assembly is housed in a concrete structure. A liquid coolant is pumped into the reactor vessel to remove heat from the core. The coolant is then pumped out of the reactor vessel and is used to produce steam. Most of the nuclear plants in the United States use ordinary water as a coolant. These plants are known as light water reactors (LWRs).

Fuels currently used consist of natural and enriched uranium, UO_2, UC_2, UO_2–PuO_2, and UO_2–ThO_2 as rods, plates, pellets, spheres, or pins and clad with zirconium, stainless steel, or other alloys. Heat is carried away from the reactor core by pressurized water, steam, sodium, helium, or CO_2. Organic liquids and molten salts have been tried but found undesirable. The heat thus removed from the core is then employed to generate steam which runs power-producing turbines, usually coupled to electrical generators. The power train is exactly similar to that used for power generation when the steam produced comes from coal, oil, or gas. Thirty years of experimentation have narrowed the fuel, moderator, heat remover, and liquid combinations but have not shown one set to be completely superior. The types of greatest interest are the pressurized water (PWR), the boiling water (BWR), the gas-cooled (GCR), and the liquid-metal cooled (LMR) reactors. The Canadian CANDU, which is deuterium moderated, and several graphite-moderated units are also in operation.

Figure 21.9 shows one of the many types of reactors being built, a forced circulation BWR which furnishes 420 MW_e. It was designed by the General Electric Co., Atomic Products Division. This reactor was selected as a power producer competitive in all but the lowest cost fossil fuel areas with a conventional boiler system fueled by oil or coal. PWR units in the 1100-MW range are offered by Westinghouse, Babcock and Wilcox, and Combustion Engineering Co. in the United States. France, Canada, Great Britain, and the U.S.S.R. also offer commercial units.

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[10]*McGraw-Hill Encyclopedia of Science and Technology*, vol. 11, McGraw-Hill, New York, 1966.

[11]Foster and Wright, *Basic Nuclear Engineering*, 3d ed., Allyn and Bacon, Boston, Mass. 1977.

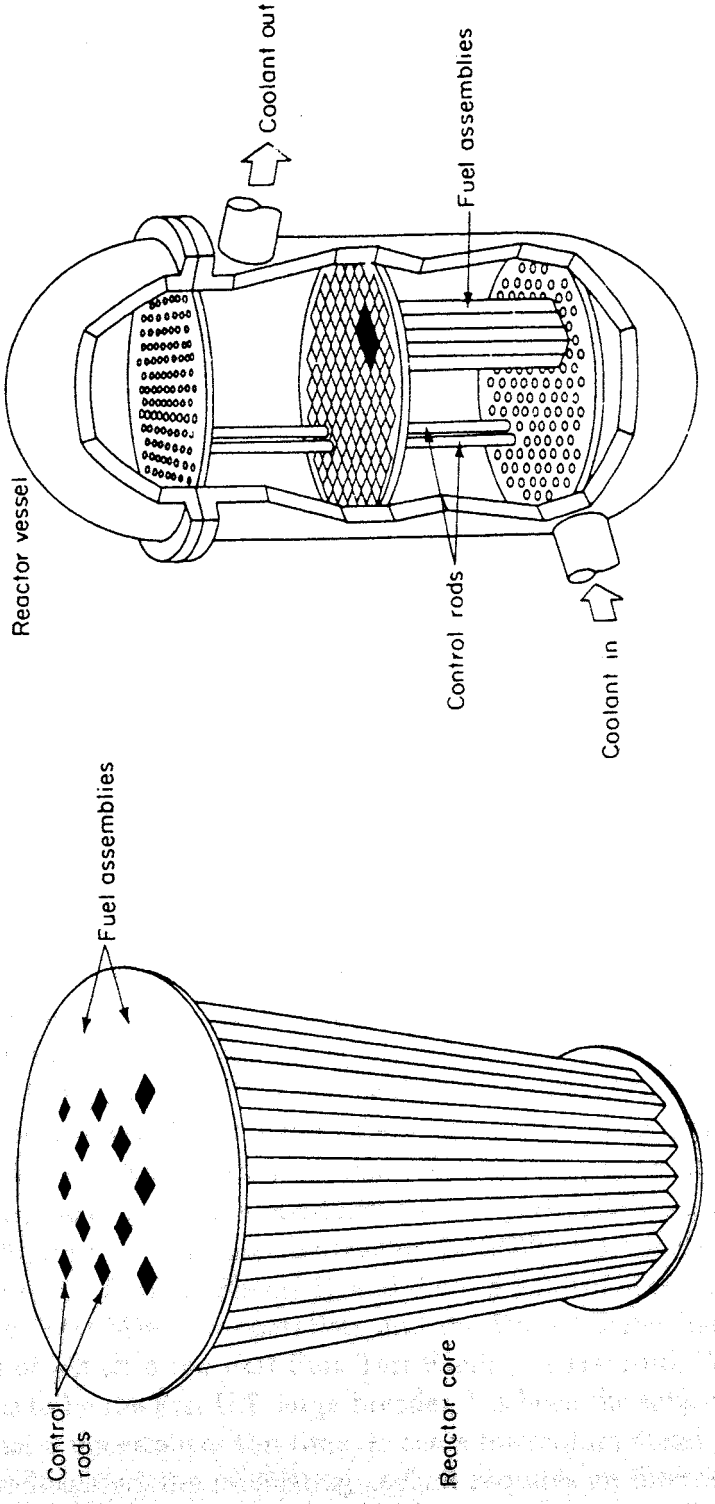


Fig. 21.7. Reactor vessel and core. [*U.S. Department of Energy, Publication DOE/NE-0029 (1982).*]

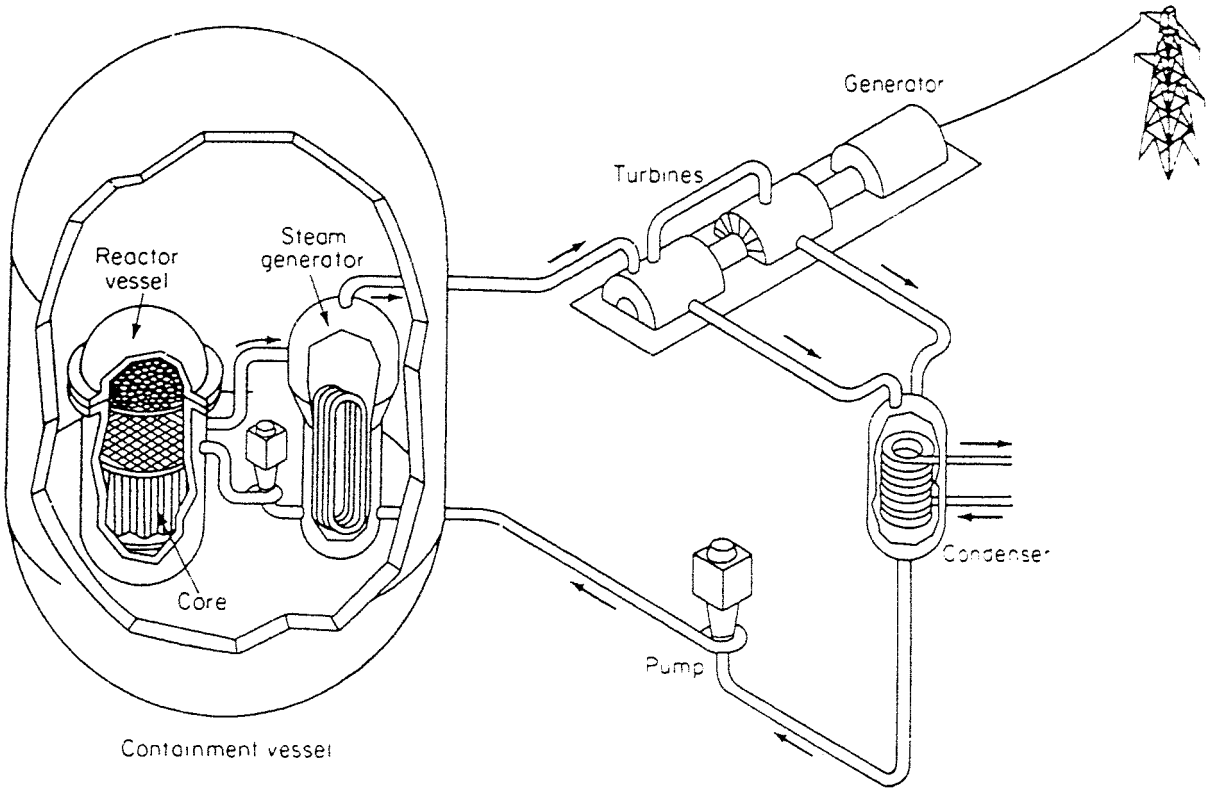


Fig. 21.8. A typical PWR (pressurized water reactor) system. In the pressurized water reactor, the pressure is kept high enough to prevent boiling, even though the water is very hot. The heated water from the core is pumped into a steam generator. Here the heat is transferred to another system and steam is produced. The water from the core is repeatedly circulated through the primary loop, but is never converted into steam. [*U.S. Department of Energy, Publication DOE/NE-0029 (1982)*]

BREEDERS.[12] Breeders are designed to produce more fuel than they consume. Breeders run without moderators, so the speed of their neutrons is nearly that at which they are expelled after fission. The probability of absorption in the central or core area is small, so the core is surrounded with a blanket of fertile material, usually ^{238}U to absorb the fast neutrons. Fission produces surplus fast neutrons which react with the surround of fertile ^{238}U which then decays to produce plutonium, suitable as a fuel after it has been extracted. Fast reactors are cooled with liquid metals (Na, NaK) because water has relatively poor heat-transfer capability and absorbs too many neutrons. Some combinations are particularly suitable for breeding. The sodium-cooled liquid-metal fast breeder reactor (LMFBR) is particularly favored. The United Kingdom (Dounreay), France (Phenix I), and the U.S.S.R. (BN-600) have several breeders of good size (up to 1600 MW_e) in operation, and the United States has several test units, the most important of which is the Fast Flux Test Facility at Hanford, Wash. The Clinch River reactor, which is to be the first U.S. large breeder, has been the subject of much controversy, and its fate remains uncertain at this time. Because the sodium metal used to cool the reactor core becomes radioactive, the circulating coolant requires an intermediate loop to prevent the escape of radioactivity into the steam loop (see Fig. 21.10). This adds to the cost and complexity of the system, but requires no new technology.

[12]O'Sullivan, Western Europe Pushing Ahead to Develop Fast Breeder Reactors *Chem. Eng. News* **56** (7) 41 (1978); Lepkowski, U.S.S.R. Reaches Takeoff in Nuclear Power, *Chem. Eng. News* **56** (45) 28 (1978).

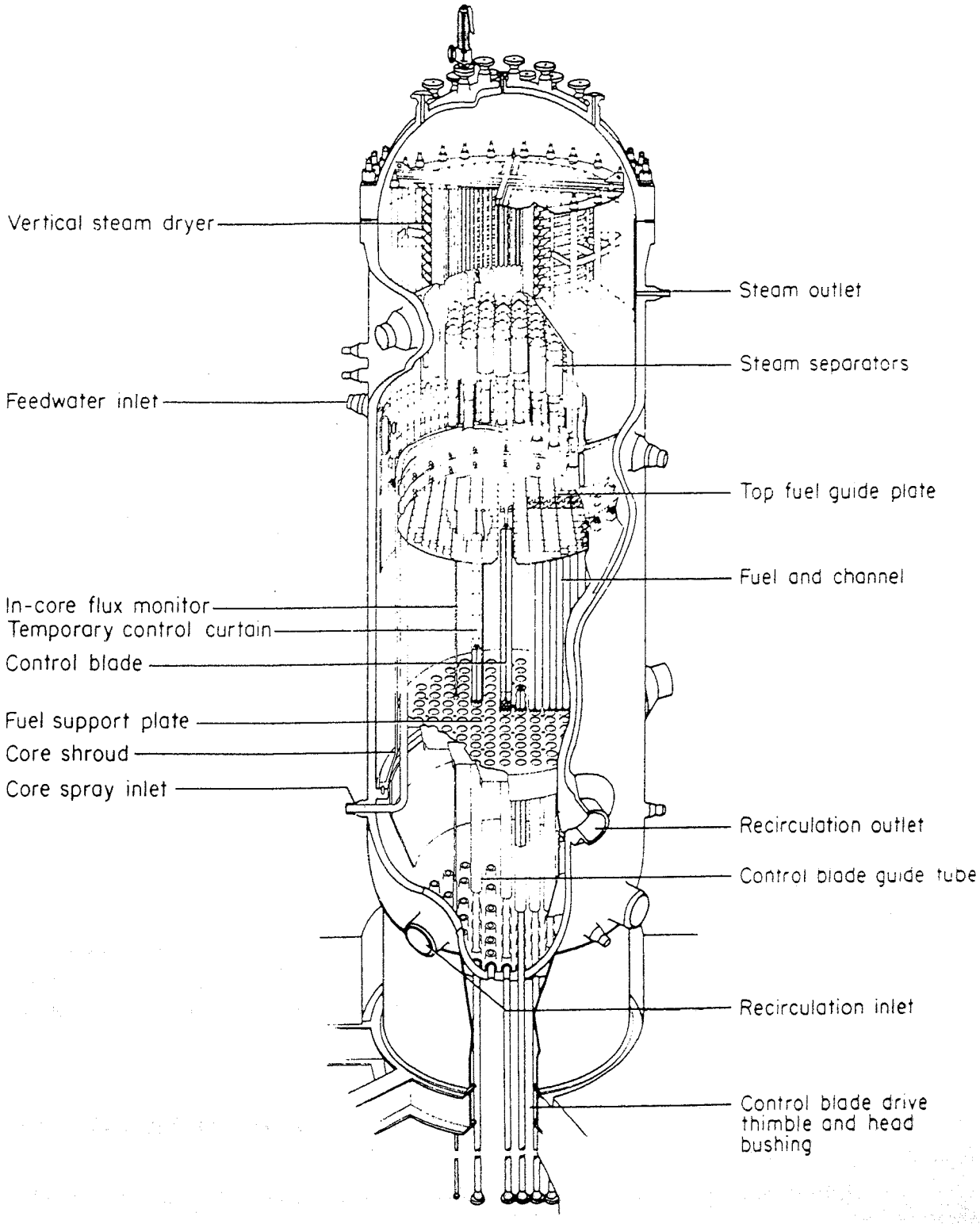


Fig. 21.9. BWR (boiling water reactor) with forced recirculation. Feedwater enters the vessel at the top of the core and, joined by recirculating coolant, flows downward around the core. The recirculation flow, which affords primary control of the load, is fed from the vessel to external pumps, which return it to the bottom of the vessel and up through the core. The generated steam passes through the internal steam separators mounted over the core, through the vertical steam driers, and then from the reactor vessel to the steam turbine. The fuel assemblies are located approximately midway in the reactor vessel. The mechanically driven control rods enter from the bottom of the reactor. The pressure vessel is 5.4 m in diameter and 17.8 m long and has a wall thickness of 18.7 cm.

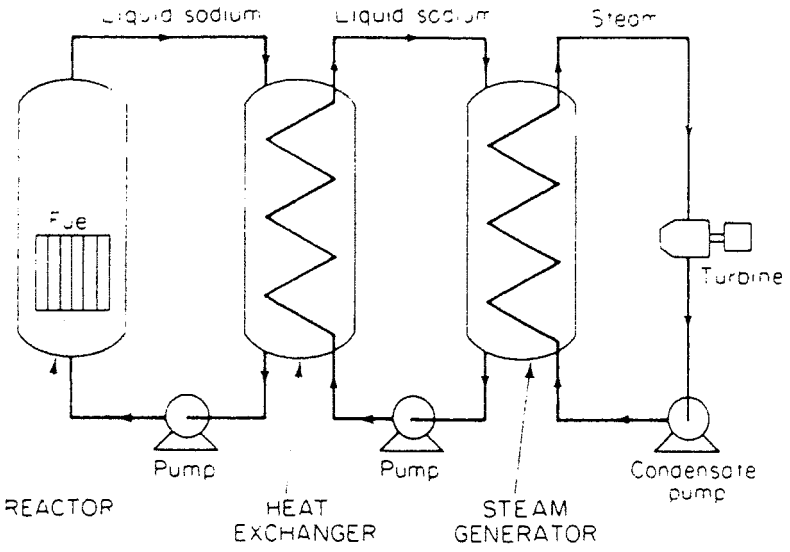


Fig. 21.10. Loop system for fast breeder reactor

The gas (helium)-cooled fast reactor requires no intermediate loop to isolate the coolant from the power stream cycle, but heat interchange is more difficult when gas is used. Operating temperature of this type of reactor is high.

Breeder reactors require chemical processing of a great deal of radioactive material, an expensive process which, among other problems, makes their use for the production of electrical power questionable economically.

CONVERTERS. Converters use ^{238}U as a fertile material to produce ^{239}Pu and are usually not designed to produce useful heat. Cores are smaller and have a longer life than power-producing units. Most military production units are of this type.

ATOM BOMBS. Atom bombs are designed to produce enormous amounts of energy in a very brief time. Fissionable materials are driven into a compact mass by explosive force, irradiated with many neutrons, and held together as long as possible, thus producing large blast effects.

FUSION REACTIONS

The conversion of hydrogen to helium converts matter into energy. For example:

$$^{1}_{4}H \rightarrow {}^{4}He + 26.7 \text{ MeV or } 4.3 \times 10^{-12} \text{ J}$$

This reaction, which takes place continuously in the sun, is being attempted by physicists. Actual nuclear fusion is more complicated than the simple reaction shown here. The energy produced is very great: 792×10^{6} MJ per kilogram of hydrogen converted. Short bursts of power have been obtained in advanced fusion apparatus, but a reaction sustained enough to permit significant power production has not been achieved. This development appears uncertain and may be many years away.

FUSION[13]

While not yet a commercial part of nuclear technology, fusion of atoms to form more complex ones can be accompanied by loss of mass with the consequent generation of energy. A great deal of expensive experimentation has as yet failed to discover a fusion system in which there is a usable net generation of energy. Scientists feel that real progress is being made, however.

The most promising fuels are deuterium and tritium, sources far less limited than uranium, thorium, oil, or coal. Fusion-fission units have also been suggested. With such units, neutrons from a fusion reactor are used to breed ^{239}Pu from ^{238}U or ^{233}U from thorium. A blanket containing fertile material, kept below critical size, would breed fissile material for use in thermal fission reactors.

PROCESSING NUCLEAR MATERIALS[14]

Since the original intent of nuclear reactors was to produce plutonium for military purposes, procedures for separating uranium and plutonium from the radioactive fission products present in spent fuel elements were developed early. These are processes involving solution of fuel elements as nitrates and separation using tributyl phosphate solvent (Purex process), or the obsolete redox process using methyl isobutyl ketone (hexone). There is also a Thorex process for thorium cycle units. Fuel elements from military production units differ markedly in Pu content from spent power units, but a typical spent fuel element from a reactor contains only 0.8% ^{235}U and a roughly similar amount of ^{239}Pu, so a large quantity of material must be handled to produce very little product. The expensive element sheath is destroyed and cannot be reused. A substantial range of isotopes, both stable and radioactive, are present. Many species present are radioactive. Currently recycling is only marginally acceptable politically and perhaps economically, but it is not likely to remain so. To prevent proliferation of nuclear weapons, the United States has taken a stand against fuel reprocessing, which may well prove economically difficult to maintain.

The flowchart of Fig. 21.11 describes the recovery plant of the U.K. Atomic Energy Authority at Windscale which uses the TBK-Kerosene process. After being dissolved in aqueous HNO_3, the fission products are separated by extracting the uranium and plutonium nitrates in an organic solvent, tributyl phosphate (TBP) and kerosene. This leaves the fission contamination products as "aqueous raffinate to the evaporator plant." The second solvent extraction is mainly for the separation of uranium from plutonium; it is effected by adding ferrous sulfamate to reduce Pu^{4+} to Pu^{3+}, a cation unable to from strong complexes with TBP and consequently removed from the organic uranium stream. The aqueous plutonium solution is oxidized to the Pu^{4+} stage (HNO_3 and $NaNO_2$), so that plutonium can be extracted

[13]Kulcinski and Burleign (eds.), *The Technology of Controlled Nuclear Fusion*, vol IV, NTIS, U.S. Dept. of Commerce, 1976; Choi (ed.), *Engineering Problems of Fusion Research*, vols. 1 and 2, IEEE, Piscataway N.J., 1981.

[14]Addinall and Ellinton, *Nuclear Energy in Perspective*, Kogan Page, London, 1982.

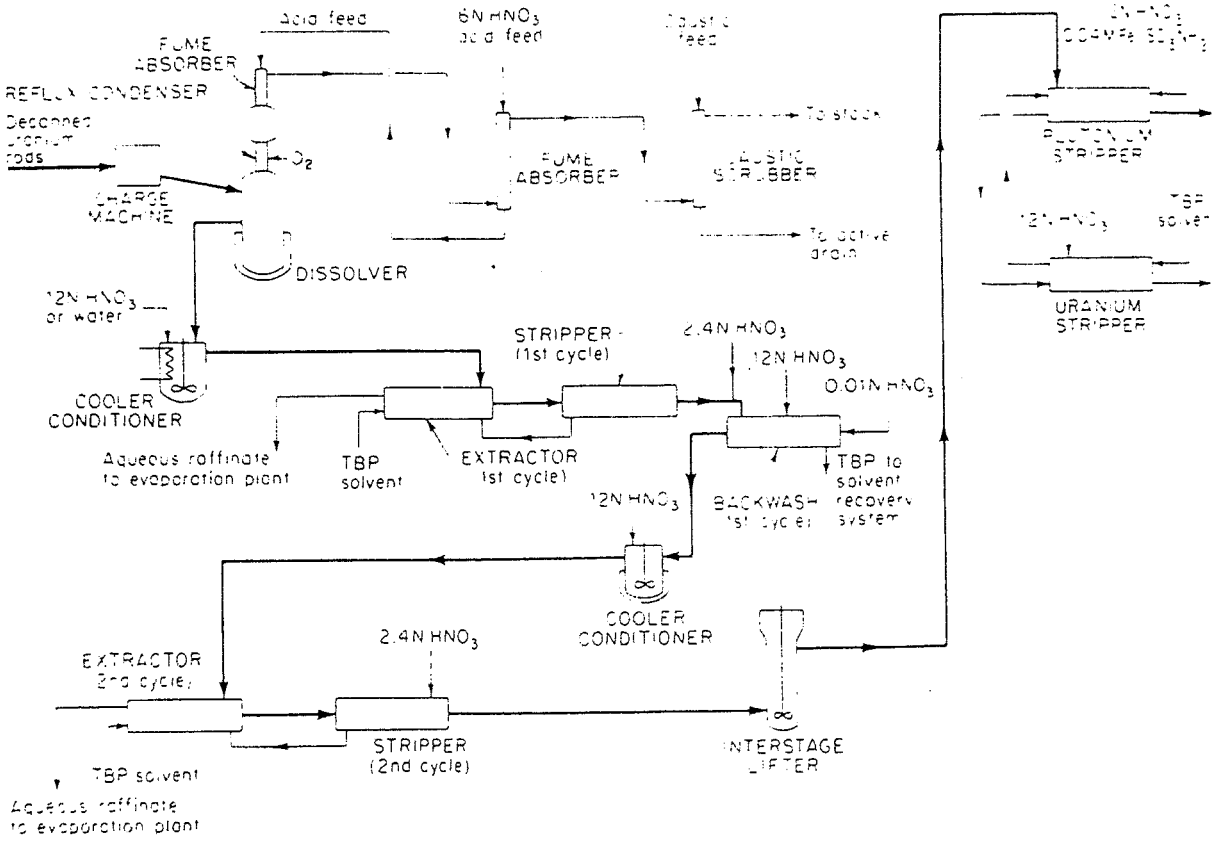
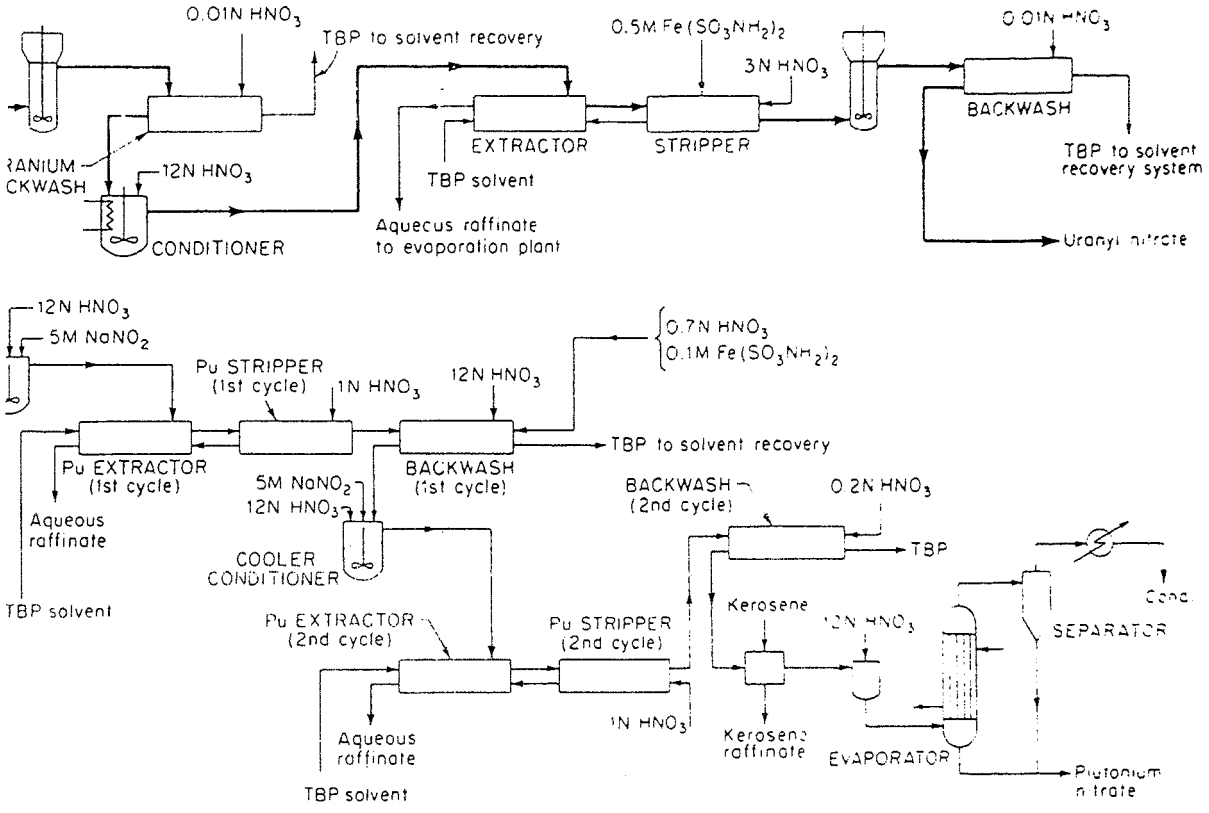


Fig. 21.11. Plutonium and uranium separation via solvent extraction from spent nuclear fuels. [*For Details, see Chem. Eng.* 71 *(25) 148 (1964).*]

with TBP from its residual fission products (aqueous raffinate). Successive acidification-oxidation and solvent extraction, followed by a kerosene washing evaporation, furnishes a pure solution of plutonium nitrate. Uranium purification, after separation from the Pu^{3+}, transfers the still impure uranium in the TBP stream by an extractive "backwash" into a dilute HNO_3 aqueous solution, and the TBP is recovered. Next another TBP extraction is used to remove uranium after a 3 *N* HNO_3 acidification, and a second ferrous sulfamate reduction to remove traces of water-soluble impurities (plutonium, etc., as "aqueous raffinate to evaporation plant"). Finally, extraction from the TBP solvent with a 0.01 *N* HNO_3 solution results in a pure aqueous solution of uranyl nitrate, which is denitrated to UO_3. Such processes require extreme precautions to protect the persons working around them from radiation hazards and use several feet of dense concrete to protect the workers. Work within such units (called cells) is frequently carried out by remote control.

There are currently no commercial reprocessing plants[15] in the United States, although one is built but unlicensed. Several foreign countries, Belgium, France, Federal Republic of Germany, U.K., India, Italy, Japan, and the U.S.S.R. operate such units. There is fear that plutonium from such plants may fall into the hands of terrorist groups or hostile nations, which restricts their construction.

[15]O'Donnell, Sandberg, and Brooksbank, Restoring Commercial Reprocessing in the United States, *Nucl. Eng. Int.* **27** (331) 30 (1982).



ISOTOPES[16] AND ISOTOPE SEPARATION

The existence of stable isotopes was known before nuclear technology developed, but the nuclear industry has given great impetus to isotope separation and use. Nuclear reactor transmutation ability has made isotope manufacture almost commonplace. Major isotopes isolated are: ^{235}U, D_2O for use as an efficient moderator, ^{10}B for reactor control and safety rods, ^{90}Sr and ^{137}Cs for food and sewage sterilization, and tritium and ^{85}Kr for compact portable light sources. The list is long and growing longer as defense wastes are studied in detail. Defense wastes are the residues from the defense production cycle.

Production of isotopes by planned transmutation is possible, but economical processes for large quantities more frequently involve the separation of naturally occurring elemental mixtures or their extraction as by-products. Defense wastes have come under study as isotope sources for several reasons: (1) The material is present and troublesome to store, (2) the storage problem can be reduced if certain strong heat and/or radiation emitters are isolated and handled separately and, (3) they are a treasure house of materials rare or absent in nature for which important uses may exist. Separation of isotopes is more difficult than ordinary chemical processes, but several techniques are well established. Substantial quantities of isotopes are separated by distillation, chemical exchange, electrolysis, gaseous diffusion, gravitational processes, thermal diffusion, and aerodynamic (nozzle) processes. Other processes known to bring about separation, but now too costly or not yet developed include, photochemical,

[16]Villani, Isotope Separation; American Nuclear Society Monograph, American Nuclear Society, Hinsdale, Ill., 1976.

photophysical laser processes, chromatography, adsorption, and electromagnetic and biological processes.

DEUTERIUM. Deterium has been in great demand and is made on a large scale. As D_2O, its current price is around $250 per kilogram. Catalytic exchange between hydrogen and water, electrolysis, distillation of liquid hydrogen, exchanges with NH_3 or H_2S, and several other separative processes have been used. Deuterium-producing plants are usually captive to ammonia-producing units because of the availability of large quantities of hydrogen.

^{10}B. ^{10}B occurs naturally at 19.8% concentration and is concentrated to 40 to 95% for control rod use by multistage exchange distribution of the weak dimethyl ether complex with the trifluoride. The price is $4 to $9 per gram of contained ^{10}B.

^{7}Li. ^{7}Li occurs naturally at 92.6% and is concentrated by a method that is currently classified. It sells for about $3 per gram of contained ^{7}Li. Minor quantities of $^{7}LiOH$ are produced because its low affinity for neutrons makes it desirable for the control of the pH of reactor water.

TRITIUM. Tritium, ^{3}H, is made in heavy-water-moderated reactors by the reaction

$$^{6}_{3}\mathrm{Li} + {}^{1}_{0}n \rightarrow {}^{3}_{1}\mathrm{H} + {}^{4}_{2}\mathrm{He}$$

It is also made by distillation of liquid hydrogen. It is of great interest in nuclear fusion work because its major fusion reaction occurs at a low temperature compared with other substances.

MISCELLANEOUS ISOTOPES. Isotopes may be used as tracers, for studying structural chemistry, in biological, chemical, and physical research, and for geological studies. ^{60}Co is used to sterilize hospital medical supplies, foodstuffs, and sewage. ^{90}Sr and ^{137}Cs are also useful because they emit sterilizing radiation. Tritium and ^{85}Kr can be used to provide lights that will function for a long time in remote locations and that require no external source of power. Palladium, rhodium, and ruthenium are also present in substantial quantity in defense wastes and may be economically recoverable.[17] Tracer elements are experimental tools of exceptional diversity and application.

PROTECTION FROM RADIOACTIVITY[18]

Radiation hazard is a subject often approached from a highly emotional point of view, probably because radiation cannot be detected by the ordinary human senses. Protection against radiation is possible with insulation (dense concrete, etc.), just as is presently done for hot

[17]Jensen, Rohrmann, and Perrig, address before American Nuclear Society, June 1980.

[18]Roussin, Abbott, and Bartine (eds.), *Nuclear Reactor Shielding*, Science Press, New York, 1977.

steam pipes or dangerous electrical conductors. Radiation is always present (background) and is released in substantial quantity by such processes as coal burning and ordinary mining. The International Atomic Energy Agency (IAEA) notes[19] that no serious radiation-induced injury or radiation-induced death has taken place at any nuclear power plant since the first nuclear power reactor went critical in 1956. This is a remarkable record considering that 274 nuclear reactors, representing 2500 reactor-years of operating experience, were in operation in 1982. Coal mining, or even riding in an automobile, is far more hazardous than working in a nuclear establishment. More than 800 nuclear installations around the world have safeguard agreements with the IAEA. This is 98 percent of the nuclear installations outside the nuclear weapons states.

The contamination of gases, liquids, and solids by substances emitting alpha, beta, and gamma radiation are all possible and must be guarded against. Shielding of only a fraction of an inch of ordinary material stops alpha and beta particles, but shielding against gamma radiation and neutrons requires massive quantities of dense materials such as heavy concrete, lead, steel, borosilicate glass, or around 7 m of ordinary water. Of course, shielding is not the only problem, containment must also be considered. Gases must not be allowed to escape, and active materials must remain isolated behind the shields in order for them to be effective. ^{90}Sr and ^{137}Cs (fission fragments) are troublesome because of their moderate half-lives (28 and 30 years, respectively). This is because living organisms tend to concentrate these isotopes selectively from dilute solutions. Unless such materials are excluded from discharge into public waters, they may enter the food chain. This phenomenon is not limited to nuclear isotopes; biological concentration of mercury was the cause of Minimata disease, which led to the outlawing of mercury cell caustic-chlorine manufacture in Japan. Despite these problems, good reliable solutions to the containment problem exist and a recent safety congress[19] concluded "there is no factor relevant to safety that limits the use and development of nuclear power."

WASTE DISPOSAL[20]

The disposal of nuclear waste presents problems, but most are now political rather than technological. Some radioactive materials must be stored for centuries until they decay to harmless materials, others rapidly become harmless.

The volume of waste to be disposed of is surprisingly small. Temporary storage in tanks permits short half-life materials to decay. Liquids can be concentrated or their dissolved solids absorbed in ion-exchange resins, converted into concrete, or glassified, permitting storage in caves, salt mines, deep wells, or the ocean. By removing long-lived isotopes for separate handling, contractors can greatly reduce the storage time for most nuclear waste. It now seems probable that, with proper management, most nuclear wastes will become harmless within 100 years. The quantity requiring geologic storage can be extremely small. The United States does not favor burial at sea because of the possibility of damage to the ecosystem and the expense of deep sea recovery, if necessary. Other countries, however, continue this practice.

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[19] *IAEA Annual Report*, 1980.

[20] Rochlin, Nuclear Waste Disposal: Two Social Criteria, *Science* 195 23 (1977).

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Chapter 2

Wood-Derived Chemicals

Each year nearly 200×10^6 t of wood are harvested from the nation's forests.[1,1a] Approximately 30×10^6 t are discarded as tree tops, stumps, roots, or scrapped logs. Half of the harvested roundwood is converted into lumber, poles, and similar wood products. The remainder is converted into pulp and paper. Wood processors classify wood into two groups. (1) hardwoods, which come from deciduous trees, and (2) softwoods, which come from conifers. The actual hardness or softness of the wood is irrelevant. Wood is a splendid, renewable resource and very valuable, but waste is enormous. It has been suggested[2] that biomass must be handled like any other valuable product: everything must be sold except the sound of the tree falling. Many new products are technically, but not economically, feasible.

Underutilization of wood products arises from the complexity of the material, lack of integration of chemical, pulp, and lumber companies, disinterest of processing companies in producing and selling by-products, lack of chemical knowledge or interest, and the dilute form in which many of the by-products are available. Since environmental laws have made the stream dumping of pulp-mill waste products impossible, some real interest in waste use has developed, but most such envisioned uses are as fuel. As the price of petroleum products rises, sylvichemicals become more enticing, but the chemistry is more complex than that necessary for petroleum processing. The use of wood as a fuel seems undesirable for such a complex raw material.

The solid portion of wood is over 95% organic.[3] It is a mixture of three groups of polymers: (1) cellulose, which is approximately 45% of the dry weight in an ordered array of high molecular weight glucose polymer chains, currently most valuable as fiber; (2) hemicellulose (20 to 25%) is a disordered array of several sugar polymers for which there is currently no economical use except as fuel; (3) lignin (20 to 25%), which serves as binder for the cellulose fibers, is a complex amorphous polyphenol polymer. Wood also contains extractives—organics removable with inert solvents. These extractives vary with the species and the location in the tree; they vary from 5 to 25% by weight and constitute several classes of chemicals. Table 32.1 shows average values for the composition of U.S. wood. Pentosans are aldopentoses formed by the hydrolysis of high molecular weight polysaccharides.

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[1]t = 1000 kg.

[1a]Goldstein, *Organic Chemicals from Biomass*, CRC Press, Boca Raton, Fla., 1981, Chap. 1.

[2]Myerly, Nicholson, Katzen, and Taylor, The Forest Refinery, *CHEMTECH* 11 (3) 186 (1981).

[3]Browning (ed.), *Chemistry of Wood*, Wiley-Interscience, New York, 1963.

Table 32.1 Composition of Wood

	Softwood,%	Hardwood, %
Holocellulose	66	76
α-Cellulose	46	49
Pentosans	8.5	19.5
Lignin	27	21

SOURCE: *Chemistry in the Utilization of Wood*, Pergamon, Oxford, 1967.

There is a great potential for novel industrial uses for wood, but the chemistry will be difficult. Use as fuel is being urged these days.[4] A ton of green wood or bark generates 18,986 MJ on combustion. Since one of the major problems in wood use is its collection and transportation out of difficult terrain to the place in which it is desired, use of waste wood is particularly attractive at lumber and pulp mills, where these chores are already done. Pulp mills derive over 40 percent of their energy needs from wood residues, and this percentage is increasing. Since the pulp and paper industry is the largest manufacturing consumer of fuel oil, the saving is important.

The derivation of chemicals from wood is an old practice. Potash from wood ashes and tannin from the chestnut tree were mainstays of commerce of the U.S. colonies and the Republic for two centuries.

HARDWOOD DISTILLATION

Charcoal was a valued commodity in antiquity. The ancient Egyptians used the volatile product of hardwood distillation, pyroligneous acid, for embalming. Before synthetic organic chemistry became well established, destructive hardwood distillation provided several important industrial chemicals,[5] among these were acetone, acetic acid, and methanol (still often referred to as wood alcohol). Charcoal is a fine, smokeless fuel, prized for its smokelessness and used extensively for outdoor cooking. Approximately 320,000 t of charcoal are produced yearly in the United States from about 1.4×10^6 t of nonmerchantable wood. Acetone was originally made by the dry distillation of calcium acetate made from wood-derived acetic acid, but better, cheaper sources are available now.

NAVAL STORES

PRODUCTS AND ECONOMICS. The days of wooden ships are past, but the use of pitch and rosin in the navy has attached the name naval stores to the extractable products from various species of pine. Gum naval stores (resin acids, called rosin, and turpentine) are obtained from the gum (oleoresin) collected from tapped pine trees. This labor-intensive source is small and

[4]Tillman, Sarkanen, and Anderson, *Fuels and Energy from Renewable Resources*, Academic, New York, 1977; Vogt; *Energy Conservation and Use of Renewable Energies in the Bio-Industries*, Pergamon, Oxford, 1981.

[5]Goldstein, op. cit., chap. 5.

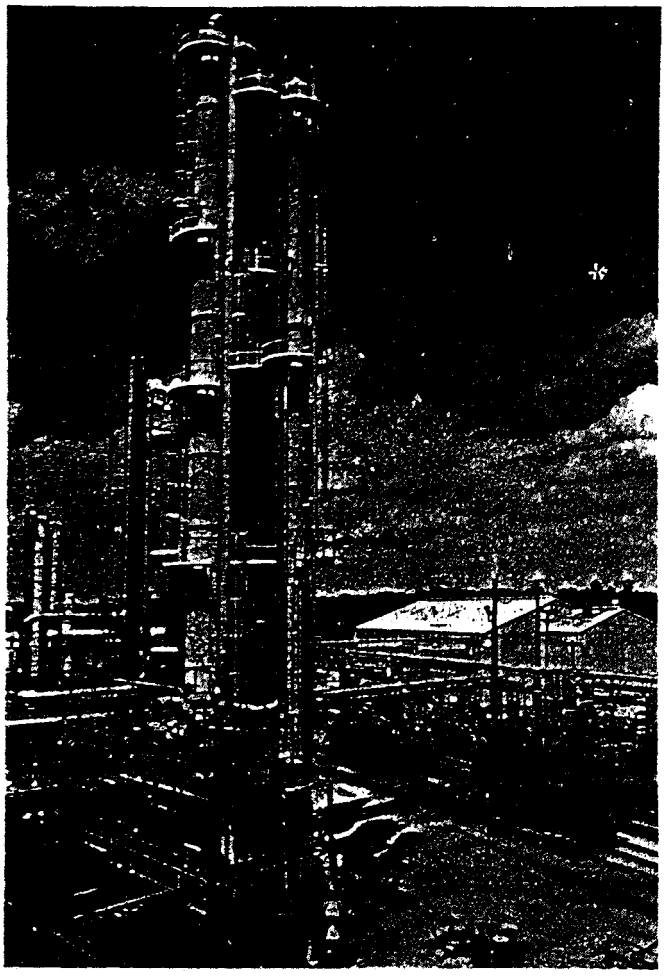


Fig. 32.1. Turpentine fractionating complex located in Jacksonville, Fla. This is capable of handling over 36,000 t annually. The basic raw material, crude turpentine from kraft paper mills, is first split into α-pinene and β-pinene. These compounds are then made into many products, such as pine oils, rosin oils, and chemicals for perfume, flavor, and pharmaceutical uses. *(Glidden-Durkee Division of SCM Corp.)*

diminishing. Wood naval stores (rosin and turpentine) are obtained by solvent extraction of pine stumps with inert solvents. Sulfate naval stores (rosin, turpentine, and fatty acids) are obtained from tall oil, a by-product of kraft pulp manufacture (Chap. 33). Resin acids are principally monocarboxylic diterpenes, and rosin is a natural mixture of resin acids. Turpentine is a mixture of monoterpenes. Fig. 32.1 shows a turpentine fractionating complex.

The sources and annual production of naval stores are given in Table 32.2 and Fig. 32.2. The major source is the kraft pulp industry. The annual production of these materials has remained fairly constant for some years, but the end uses of the materials have changed drastically. Figure 32.3 shows a flowchart for naval stores from stumps and gives the usual

Table 32.2 Naval Stores Consumption
(in thousands of metric tons)

	Turpentine			Rosin		
	1973	1978	1979	1973	1978	1979
Chemicals and rubber	71,364	81,084	81,228	135,558	85,346	83,355
Ester gums and synthetic resins	—	—	—	62,727	54,949	63,172
Paint, varnish, and lacquer	136	106	67	11,818	4,582	5,105
Paper and paper size	182	—	—	81,818	109,273	83,087
Other	590	1270	1,009	12,273	21,105	16,1901
Total	72,272	82,460	82,304	304,194	275,255	250,909

SOURCE: *U.S. Agricultural Statistics*, 1981.

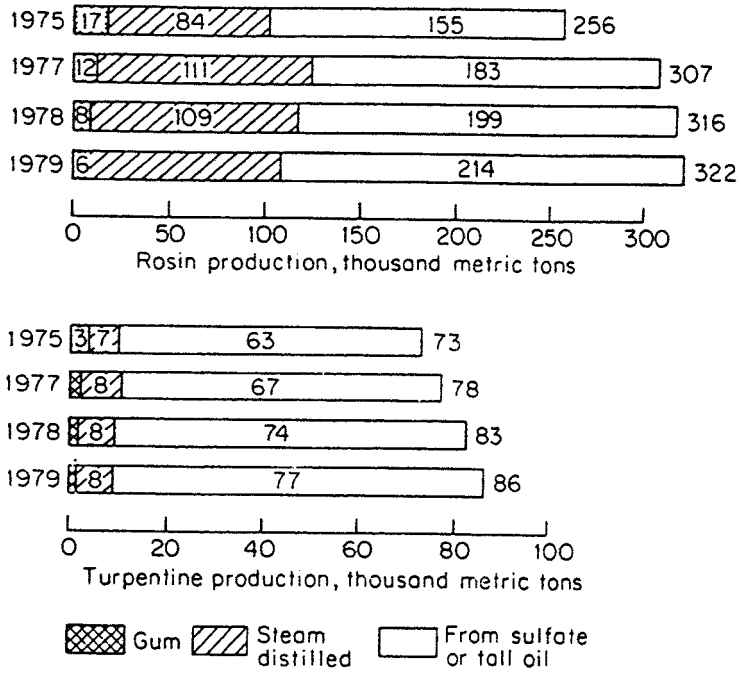


Fig. 32.2. Naval stores production.

distribution of products. Naval stores were exported to England as early as 1608, coming originally from New England, but rapidly replaced by North Carolina and Georgia. Florida and Georgia are presently the major producers of gum turpentine, but compared with other sources, gum production is small. Tall oil is now the major source.

MANUFACTURE OF NAVAL STORES

Gum Oleoresins. Gum is obtained from the pine trees by cutting (slashing) them and sometimes by treating the slashes with chemicals, and then collecting the exuded oleoresin by hand, a slow and expensive process. Separation is by steam distillation.

Steam and Solvent Process. Cut-over pine forest stumps and trash wood provide the raw material. Figure 32.3 shows the essential steps:

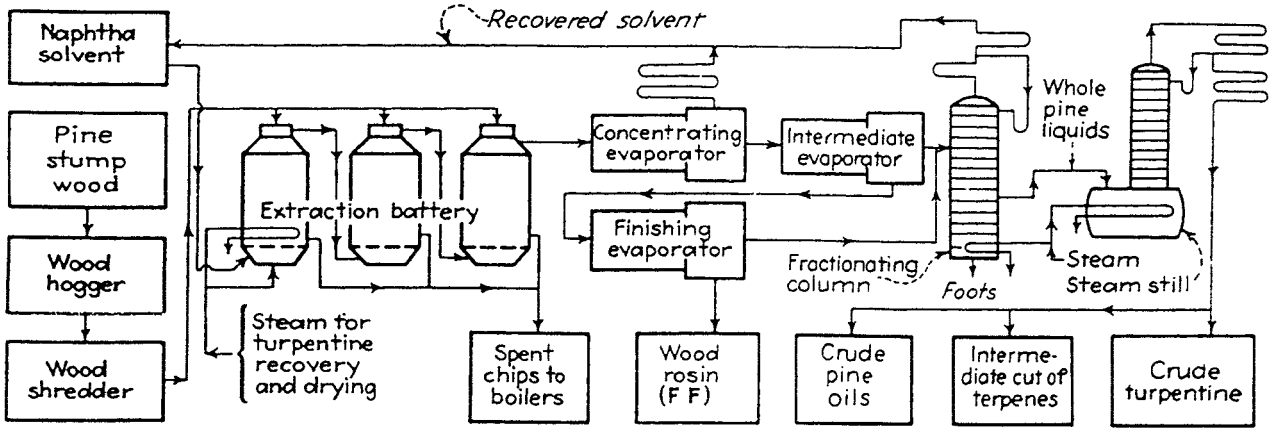
The wood is first ground in a wood hog and then reduced to splinters in a shredder.

The chips are loaded into a battery of extractors, where they rest upon a false bottom, below which live steam under pressure is admitted at the end of the run for solvent recovery. The extractors are built of acid-resistant stainless alloys and operate at pressures of 446 to 584 kPag.

The solvent (so selected that it is easily separated from turpentine) countercurrently extracts the chips. This solvent may be naphtha or a petroleum fraction with a boiling range of 93 to 116°C. The hot solvent is drained off, and the residual material on the chips is removed by subsequent steam distillation. The chips are used for fuel.

Most of the solvent is removed from the turpentine, pine oil, and rosin in a concentrating evaporator.

The residue from the first evaporator is sent to an intermediate evaporator. The vapors from this evaporator are led into the upper part of the continuous fractionating column, and the residue is sent to the finishing evaporator.



From 1000 t of white pine can be obtained (in liters):

Turpentine, 155–167°C	21,910	Pine oils	20,790
Intermediate turpene*	11,230	Tar	2,250
		Total crude oils	56,185

**Included herein are the hydrocarbons: p-menthane, dipentene, p-cymene, terpinene, and terpinolene.*

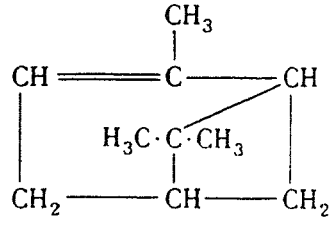
Fig. 32.3. Flowchart for wood rosin and turpentine production by steam and solvent extraction.

Vapors from this final evaporator are combined with those of the intermediate evaporator before entering the fractionating column.

Residue from the third evaporator is whole-wood rosin and may be treated by selective solvents and certain absorbents such as fuller's earth to yield light rosins.

The continuous fractionating column separates the pine oils and turpentine from the last of the solvent. Pine liquids from the continuous column are separated into three fractions in a batch still: crude pine oil, an intermediate cut of terpenes, and crude turpentine. Careful fractionation of these three cuts produces many marketable products.

TURPENTINE. Turpentine is a mixture of organic compounds known as terpenes. An example, and a major constituent, is α-pinene.[6]



Originally used as a volatile paint and varnish thinner, but undesirable because of its strong odor, turpentine has been almost totally replaced by volatile petroleum fractions (VM&P, varnish maker's and painter's naphtha). Violent swings between shortage and oversupply have hampered the industry.

[6]Terpenes, ECT, 2d ed., vol. 14, 1969, p. 803.

SULFATE PULP TURPENTINE. The relief gases from the digesters for kraft (sulfate) pulp contain turpentine and pine oil. When the gases are condensed, 8 to 40 L of oil can be separated per ton of pulp produced. This oil contains 50 to 60% turpentine and 10 to 20% pine oil; these are usually separated by distillation. Odoriferous mercaptans contaminate the turpentine. Treatment with mild oxidizing agents, such as sodium hypochlorite, or solution in ethylenediamine removes these substances.

Pine oil can be obtained by fractionating pine stump extractives, but about half is "synthetic," made by mineral acid conversion of the α-pinene in turpentine to α-terpineol. Further treatment gives the pharmaceutical, terpin hydrate. Pine oil is an odorant and bactericide in household cleaners, an odorant for a variety of other products, and a flotation agent; it is also used in processing textiles.

Low molecular weight polyterpin resins used in pressure-sensitive tapes, adhesives, chewing gum, dry-cleaning, and paper sizes are made from α- and β-pinenes and pyrolyzed α-pinene from turpentine.

Toxaphene, a valuable pesticide, has been made by chlorination of a terpene obtained from turpentine. Its use has recently been severely restricted.

A wide variety of flavors and fragrances is made by the isolation of fractions of turpentine and by chemical conversion of these fractions. These include lime, lemon, peppermint, spearmint, and nutmeg synthetic essential oils and linalool, citronellol, nerol, geraniol, menthol, and ionones as semisynthetics.[7] Some entirely new fragrances and flavors have also been prepared. Turpentine is much more valuable as a chemical raw material than it ever was as a solvent.

ROSIN. Rosin is obtained from both stump extract and tall oil processing. The availability of aged stumps is steadily diminishing and with it the competition for tall oil rosin. The demand for tall oil rosin, 220,000 t in 1979, is expected to expand to 283×10^6 t by 1989.[8] Rosin contains mainly diterpene resins such as abietic and pimaric. Rosins are generally modified before use by means of hydrogenation, esterification, reaction with formaldehyde or maleic acid, and similar processes. The use of the sodium salt of rosin in yellow laundry soap has largely disappeared. The major use is as a paper sizing agent as the precipitated aluminum salt. Esterified, it becomes ester gum, an ingredient of some varnishes. Rosin is also used in tackifiers, adhesives, chewing gum, and coatings.

TALL OIL. Tall oil is the generic name for the oil obtained upon acidification of the black liquor residue from kraft digesters. Kraft processing dissolves the fats, fatty acids, rosin, and rosin acids contained in pine woods in the form of sodium salts. When the black liquor is concentrated to make it possible to recover some of its chemical and heating value, the soaps become insoluble and can be skimmed off. The brown, frothy curd thus obtained is then made acidic with sulfuric acid,[9] converting the constituents to a dark-brown fluid called tall oil. The name is derived from the Swedish "talloja," pine oil, and has come into use to avoid confusion with pine oil from wood distillation, already an article of commerce. Fractionation under

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[7]Zinkel, Chemicals from Trees, *CHEMTECH* 5 (4) 238 (1975).

[8]Naval Stores Markets on Hold during Recession, *Chem. Eng. News* 60 (21) 30 (1982).

[9]Continuous Tall Oil Route Saves on Power and Labor, *Chem. Eng.* 79 (2) 76 (1972); How to Increase Tall Oil Output, *Chem. Eng. Prog.* 69 (9) 80 (1973); Drew, Maximizing Tall Oil Recovery, *Chem, Eng. Prog,* 72 (6) 64 (1976).

vacuum separates the crude material into its component parts. Tall oil fatty acids have enjoyed a brisk sale because, among other good properties, they are the cheapest organic acids available. United States tall oil fractionating capacity was 860,000 t/year in 1982.[10] Utilization of this material reduces waste and stream pollution. Fractionation allows for various desired compositions. Tall oil is the major source of turpentine. Tall oil fatty acids are mostly normal C_{18} acids, 75% mono- and di-unsaturated, with lesser amounts of saturated and tri-unsaturated constituents. Alkyd resins are the major market (20 percent) for tall oil, and soybean oil is its major competitor. Seven to ten percent is used in soap manufacture. There are a host of other uses, waterproofing agents, dimer acids, polyamide resins for printer's ink, adhesives, detergents, and agricultural emulsifiers, to name a few. Price is around 45 cents per kilogram.

LIGNINS AND LIGNOSULFONATES. Lignin constitutes a large percentage of the noncellulosic part of wood. Newer laboratory processes yield quality lignin with molecular weights of 200 to 1000, but kraft process lignin has a molecular weight of 1000 to 50,000 and is altered chemically by sulfonation. For years it has been realized that this should be an important source of benzenoid chemicals, but development has been slow in coming.[11] Presently it is mostly used as a fuel, but as petroleum becomes increasingly scarce and expensive, proposals and experimental plants for using this material begin to appear. One such process[12] uses fluid-bed hydrocracking and dealkylation to produce phenols and benzene

Lignin derivatives, sulfonated alkali lignin and sulfite lignosulfonates, are being used to increase tertiary oil recovery in "pumped out" oil wells,[13] replacing more expensive synthetic detergents. This could become a very large market.

High yield pulping processes and improved bleaching methods leave much more lignin in paper, which is certainly one of its most economical applications. Lignin's composition and molecular weight vary with the species of wood being used. Chemical technology concerning the fragmentation of large molecules to produce useful small ones is not nearly so well-developed as that for synthesis of large molecules from small ones. This impedes progress in finding economical processes for using lignin.

Despite these difficulties, several products made from lignin are currently profitable. Vanillin is made from sulfite waste liquor, but the available supply greatly exceeds the demand despite low yields. Dimethyl sulfide, dimethyl sulfoxide (DMSO), and methyl mercaptan are finding small but important markets. Alkaline waste liquors and lignosulfonates are sold as dust stabilizers, asphalt emulsion stabilizers, dispersing agents, binders for various substances, drilling fluid additives, etc., but the major use remains as fuel for pulp mills.

HYDROLYSIS OF WOOD

Wood, waste paper, and municipal waste contain cellulose which can be converted to sugar which can then be fermented to give ethanol, a potentially important motor fuel. This process

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[10]Turmoil in the Market for Tall Oil Derivatives, *Chem. Week* 129 (12) 29 (1981). Layman, Naval Stores Markets on Hold during Recession, *Chem. Eng. News* 60 (21) 30 (1982).

[11]Sarkanen and Ludwig, *Lignins*, Wiley-Interscience, New York, 1971; Graff, *Chem. Eng.* 89 (26) 25 (1982).

[12]Lignin Conversion Process Shows Promise, *Chem. Eng. News* 58 (44) 35 (1980).

[13]Wood Chemicals Inject New Life into Tired Oil Wells, *Chem. Week*, 124 (25) 65 (1979).

continues to attract attention because it utilizes waste materials instead of foodstuffs for its raw materials. The process was first developed in Germany during World War I and has been under development ever since. By 1941, 30 foreign plants were in successful operation producing alcohol from wood by hydrolysis with weak sulfuric or hydrochloric acid, followed by fermentation. The U.S.S.R. has a number of operating plants. Cellulose is considerably more valuable (44 cents per kilogram) than glucose (7 cents per kilogram) or ethanol, so only sources unsuitable for paper production can be considered as raw material. Straw, sawdust, corncobs, etc., are possibilities.

Until recently, most studies showed all processes suggested to be uneconomical in the United States. The increases in petroleum costs have revived interest and it appears that financially competitive processes are about to emerge.[14] The processes are in a state of flux, as described in the references, and the definitive commercial process is not yet determined.

Hydrolysis to glucose can be accomplished with weak or strong sulfuric or hydrochloric acids or with any of several enzymes which work under both high and low temperatures on separated or unseparated cellulose. Conversion of the cellulose present varies from 50 to over 90 percent, and the time required for conversion is highly variable. The final alcohol solution obtained before rectification varies from 2% to around 12%. To keep processing costs within reason, at least 5% is required. Getting hydrolyzing reagents to react with wood involves effective contact with the whole mass, so pressure systems and wood explosion techniques involving screw presses are being tried. By-product utilization is also important. Molasses for cattle feed and lignin suitable for use in plastics are to be produced, and some proposed installations are designed to only make such syrups and solids instead of ethanol. It would be very desirable to convert hemicelluloses to fermentable sugars, and some processes can do this. Figure 32.4 shows a flowchart for a currently demonstrated process designed to make dilute alcohol (commonly referred to as beer).

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[14]Hsu, Ladisch, and Tsao, Alcohol from Cellulose, *CHEMTECH* 10 (5) 315 (1980); Emert and Katzen, Gulf's Cellulose to Ethanol Project, *CHEMTECH* 10 (10) 610 (1980); Emert, Katzen, and Kaupisch, Economic Update on the Gulf Cellulose Alcohol Process, *Chem. Eng. Prog.* 76 (9) 47 (1980); Remirez, Wood-to-Ethanol Methods Edge Closer to Fruition, *Chem. Eng.* 88 (2) 51 (1981); Berry, Ethanol from Wood, *Chem. Eng.* 88 (12) 62 (1981); Worthy, Cellulose-to-Ethanol Projects Losing Momentum, *Chem. Eng. News* 59 (49) 35 (1981).

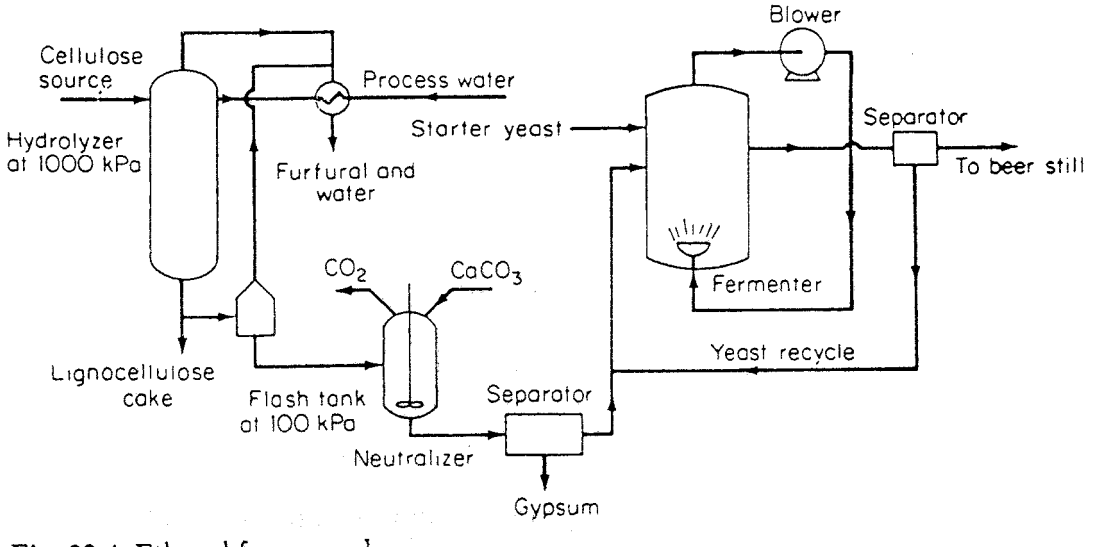

Fig. 32.4. Ethanol from wood.

Hardwoods, when used to make paper by the sulfite process, yield waste liquors containing as high as 3% sugars, principally xylose and arabinose, softwoods give only about 2% sugars, principally mannose along with mixed hexoses and pentoses. After the sulfite content of the waste liquor is reduced by steam stripping, $(NH_4)_2HPO_4$ is added to promote growth of yeast, the pH is adjusted, and the mixture added to a continuous fermenter inoculated with *Candida utilis* (also known as *Torulopsis utilis*) yeast. Aerobic fermentation ensues, controlled at 32 to 38°C by cooling coils or an exterior heat exchanger. Much foaming occurs. The fermenters are large, 8 m in diameter × 4.3 m high. Fermenter liquor containing about 1% yeast solids is removed at the same rate at which feed is added and concentrated to 5% by centrifuging. Repeated washing and centrifuging gives a solids content of 15%. This material is then pasteurized and dried in spray or drum driers. The material thus obtained is called torula yeast and contains about 47% protein and a very high vitamin content. It makes an excellent dietary supplement for animal feed, quite comparable with milk and meat.

In the sulfite process for the manufacture of pulp, sugars are formed by the hydrolysis of wood constituents that are dissolved out when producing usable fibers for paper. Approximately 65 percent of these sugars is capable of being fermented to alcohol. This is equivalent to about 1 to 2 percent of the sulfite waste liquor. First, the sulfite waste liquor is separated from the pulp and conditioned for fermentation.[15] After cooling to 30°C and adding lime (to adjust the pH to 4.5) and urea nutrient, the liquor is pumped into the fermentors and fermented. The alcohol is distilled out and rectified. In Sweden all the alcohol (and many derivatives therefrom) is based on waste sulfite liquors, including all beverage spirits and, during the war, alcohol for motor fuel.

Xylose and xylitol are being made from wood and have found a small market as sweeteners for diabetics.

WOOD EXTRACTIVES AND CONVERSION PROCESSES

Wood is the source of a large number of chemicals and pharmaceuticals, many of them produced primarily outside the United States. Tannins extracted from chestnut and oak wood, bark, and leaves were of major importance until the chestnut was destroyed by blight and the oak proved too expensive to collect. Cedarwood oil continues to be used for "cedar" chests and sassafras oil is used for flavoring. Several essential oils from twigs, barks, and fruits enjoy brisk but small sales. Gums are also obtained from a variety of trees such as tara and locust. Only one, arabinogalactan, a water-soluble gum from the western larch or tamarack (*Larix occidentalis*) is made in the United States in any quantity. Rubber is a well-known forest product. Several different trees yield oils and waxes that are articles of commerce; jojoba oil and carnauba wax are probably the best known. Quinine is from cinchona bark. Furfural is made by alkaline treatment of wood, oat hulls, or corncobs. There are a variety of spices produced in small quantities for specialty trades which are rarely thought of as chemical products.

Bark removed from trees at sawmills and pulpmills is regarded as an expensive nuisance. Some inexpensive fillers are made from bark flour, but most is burned, used as a soil improver,

[15] *Forest Products and the Environment*, AIChE Symp. Ser. No. 133, Vol. 69, 1973, p. 2

or wasted. A plant in Oregon[16] converts fir bark into a high-quality vegetable wax, a thermosetting-resin extender, and a phenol substitute. Cork and bast fiber can also be made. Much more extensive use of bark and wood by-products must be made in the future. Wood products should not be regarded primarily as fuels.

CELLULOSE DERIVATIVES

The most important cellulose products are pulp and paper, so Chap. 33 is devoted to their manufacture.

Rayon, an excellent polymer of regenerated cellulose, is covered in Chap. 35 under synthetic fibers.

[16]Good and Trocino, Fir-Bark Conversion Route, *Chem. Eng.* **81** (11) 20 (1974); Burgon et al., U.S. Patent 2,880,216.

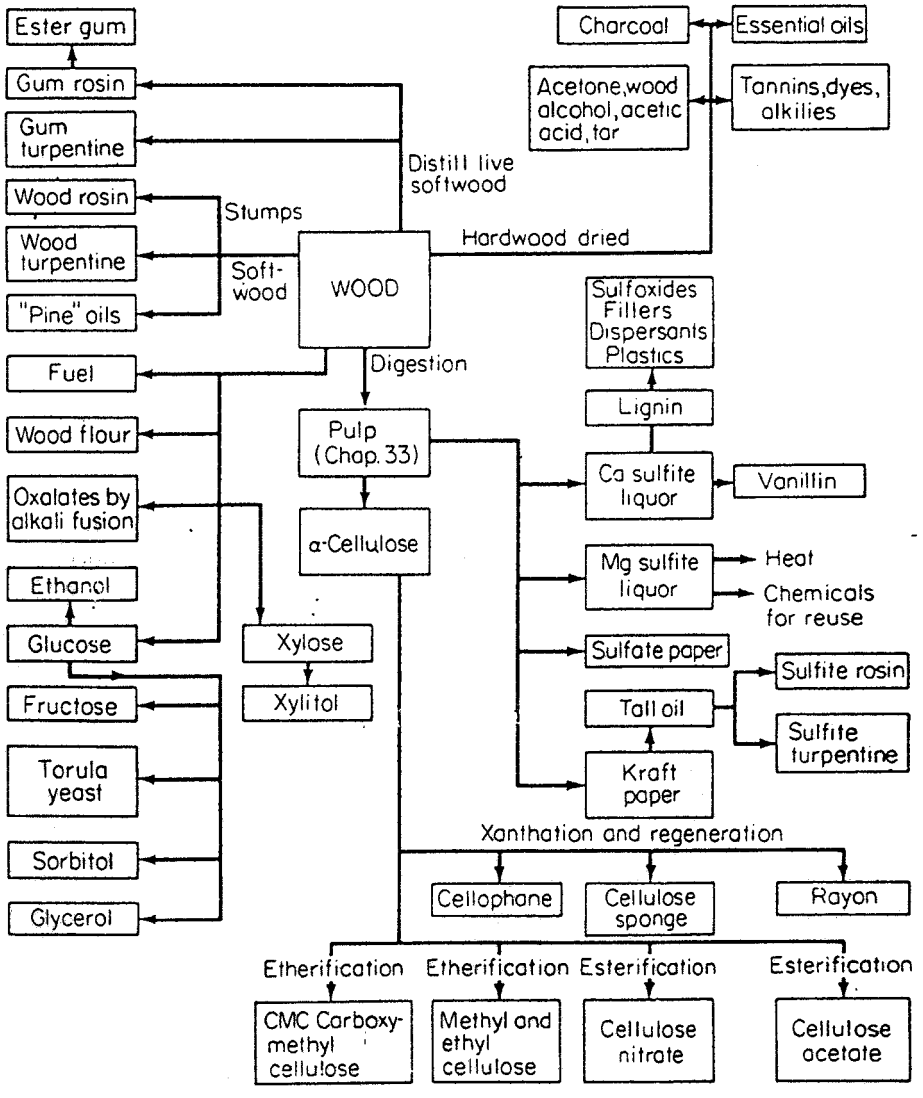

Fig. 32.5. Wood chemicals.

Highly purified cellulose, known as α-cellulose, is the basic material for the manufacture of cellulose nitrate for plastics and explosives as well as most chemical derivatives.

Many cellulose derivatives have attained commercial importance (Fig. 32.5) such as the ethers: ethyl cellulose, methyl cellulose (Dow's Methocel), and carboxymethyl cellulose. The last mentioned is frequently known as CMC and may be prepared by the following alkylation:

$$\underset{\text{Cellulose}}{[C_6H_7O_2(OH)_3]_x} + x\text{NaOH} \rightarrow \underset{\text{Alkali cellulose}}{[C_6H_7O_2(OH)_2ONa]_x}$$

$$[C_6H_7O_2(OH)_2ONa]_x + x\underset{\text{Sodium chloroacetate}}{\text{ClCH}_2\text{COONa}} \rightarrow \underset{\text{Sodium carboxymethyl cellulose}}{[C_6H_7O_2(OH)_2COONa]_x}$$

Various degrees of etherification have been commercialized. Sodium CMC is a white powder when dry, though it is generally produced and sold as solutions of varying concentration and viscosity. By 1970, CMC production had grown to more than 30×10^6 kg/year. It is physiologically inert and is employed as a protective coating for textiles and paper, for sizing, for ice cream and other emulsion stabilizers, and as an additive to impart strength to sausage casings and other films. Hydroxyethyl cellulose, a high-viscosity product, is useful as a thickener and a protective colloid in water-based coatings.

Among the many specialty products developed, cellulose sponges form an important segment. The dyed viscose cellulose sponge syrup is mixed with various-sized crystals of sodium sulfate, placed in a mold, and heated to "set" the mix around the crystals. Further heating dissolves the crystals in water (that is part of their own crystallization), after which the product is removed from the mold and washed

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Chapter 3

Man-Made Fiber and Film Industries

HISTORICAL. Fibers were originally of natural origin and were produced from wool, silk, cotton, flax, and similar materials. The first man-made fibers were made by Swan in 1883 when he squirted a solution of cellulose nitrate in acetic acid through holes. The first commercial fibers made from cellulose nitrate were produced by Chardonnet who patented his process in 1885. The next synthetic fiber was also a cellulose derivative, regenerated cellulose or viscose. Although the production of viscose was patented in 1892, it was not until 1930 that the world production had grown to 200,000 t annually.[1] This was due, in part, to the poor wet strength of the original fibers. Viscose was considered to be a cheap, poor substitute for silk until methods of increasing the wet strength were developed. Other variations of cellulose fibers were invented and introduced. Cuprammonium rayon fiber was made about 1900, and cellulose acetate fiber about 1921. Many improvements and variations have been made on these basic cellulose fibers.

The first truly synthetic fiber was nylon (a polyamide) introduced in 1940. This was discovered by Carothers and was commercialized by DuPont. The next fibers that emerged were polyesters, acrylics, and polyolefins. These four types were the principal synthetic fibers produced until the middle 1950s. During the latter part of the 1950s, and continuing to today, much research was devoted to improving the properties of the fibers and to development of fibers with special properties for particular uses (e.g., high-temperature resistant fibers).

USES AND ECONOMICS. Man-made fibers, from their humble beginning, have grown to 45 percent of the world's fiber production. In 1981, 14×10^6 t of man-made fibers was produced worldwide, and natural fibers prepared amounted to 17×10^6 t. The production of the various fibers in the United States from 1966 to 1981 is shown in Fig. 35.1.

The uses of man-made fibers depend upon the nature of the individual fiber. Clothing, carpets, and upholstery are all made largely, or wholly, of synthetic fibers. The blends of polyester and cotton have imparted ease of washability and permanent-press to shirts and other garments. Most of the nylon produced in the United States is used for carpets. Other uses will be discussed in connection with the individual fibers.

PROPERTIES OF FIBERS. Three of the more important general properties of fibers are length, crimp, and denier. Fibers are either a continuous filament or short fibers, rather uniform in length, spun into a thread. The short fibers, i.e., cotton and wool, are called staple. Continuous filaments can be of almost infinite length and most synthetic fibers, as well as natural silk, are of this type. Synthetic staple fibers are prepared by cutting continuous filaments to short, uniform lengths, usually between 3.5 and 15 cm.

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[1] t = 1000 kg.

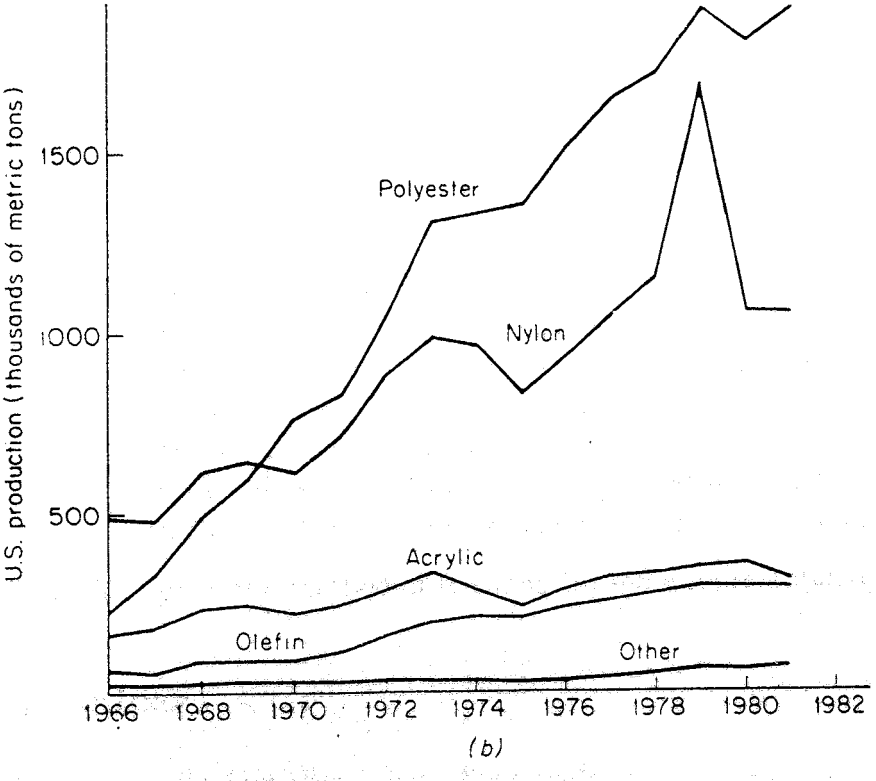


Fig. 35.1. Trends in the production of man-made fibers.

The curl, or waviness, placed in synthetic fibers by chemical or mechanical action is called crimp. It is of great importance in the processability of staple fibers. Crimp is also introduced in some cases, into continuous-filament yarns to alter their appearance and feel, e.g., in nylon carpet yarn. Cotton and wool possess natural crimp.

Denier is a measure of the weight of fibers per unit length and is defined as the weight in grams of 9000 m. Another unit is the *tex* which is the weight of 1000 m.

The first synthetic fibers were circular, but special characteristics can be imparted by manufacturing fibers with nonround cross sections. A carpet yarn, developed in Germany,[1a] has a pentagonal cross section and contains six structural holes. As light passes through the holes it is deflected and broken up and thus reduces the visibility of soil particles. The five-sided fibers also aid in soil release. Most of the fibers on the market today have filaments whose cross sections are not uniformly round.

SYNTHETIC FIBERS

CLASSIFICATION. The versatile noncellulosic fibers, whose market is rapidly growing, are classified chemically and by the method of spinning in Table 35.1. The manufacture of all true synthetic fibers begins with the preparation of a polymer consisting of very long, chain-like molecules. The polymer is spun and this results, in most cases, in a weak, practically useless fiber until it is stretched to orient the molecules and set up crystalline lattices. By controlling, within limits, the degree of orientation, crystallinity, and average chain length, a single polymer can be used to make a number of fibers with widely differing mechanical properties ranging from weak and stretchy to strong and stiff. Two elements important in determining the range of the polymer's mechanical properties are the attractive forces between the molecules and the flexibility and length of the molecular chains.

Spinning procedures are divided into melt, dry, and wet.

1. Melt spinning, developed for nylon and also used for polyester, polyvinyl, polypropylene, and others, involves pumping molten polymer through capillaries or spinnerets. The polymer streams that emerge from the spinneret openings are solidified by quenching in cool air.
2. In dry spinning, the polymer is dissolved in a suitable organic solvent. The solution is forced through spinnerets, and upon evaporation of the solvent in warm air, dry filaments are formed. Some acrylics and vinyl-acrylic copolymers are spun in this manner.
3. Wet spinning involves spinning of a solution of polymer and coagulation of the fiber in a chemical bath. As an example, a polymer dissolved in dimethyl acetamide could be coagulated in a bath of glycerol at 140°C, or coagulated in a bath of 40% calcium chloride at 90°C. Acrylics, such as Acrilan and Creslan, are prepared by wet spinning.

Table 35.1 gives the method of spinning for some representative fibers.

Polyamides

Nylon 6,6 was the first all-synthetic fiber made commercially and opened up the entire field. In 1981 the U.S. production was 1.18×10^6 t, of which 59 percent was used for home furnishings, mostly carpets. Apparel accounted for 20 percent and tire cord for 11 percent.

[1a] *Text. Ind.* 146 (9) 106 (1982).

Table 35.1 Representative Synthetic Fibers and Films*

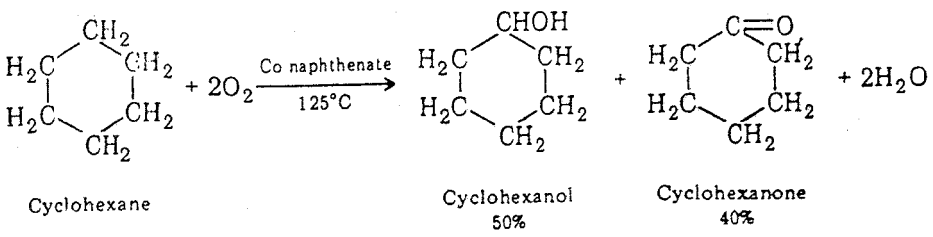
Classification	Spinning†
Polyfibers and Films	
Polyamides, or nylon, fibers	
Nylon 66, nylon 6, Qiana	Melt
Polyesters	
Fibers: Dacron, Trevira, Kodel, Fortrel	Melt
Films: Mylar, Cronar, Kodar, Estar	Melt
Acrylics and modacrylics	
Orlon fiber	Dry
Acrilan fiber	Wet
Creslan fiber	Wet
Dynel fiber (vinyl-acrylic)	Dry
Verel fiber	Dry
Vinyls and Vinylidines	
Saran fiber and film	Melt
Vinyon N fiber‡	Dry
Spandex	
Lycra	Dry
Numa	Wet
Glospan	Wet
Olefins	
Polyethylene films	Melt
Polypropylene fibers and films: Avisun, Herculon	Melt
Glass Fibers	
Fiberglass	Melt
Cellulosic Fibers and Films	
Regenerated cellulose	
Fibers: Rayon (viscose), cuprammonium	Wet
Film: Cellophane	Wet
Cellulose esters	
Acetate fibers and films: Acele, Estron	Dry
Triacetate fiber: Arnel	Dry

*Completely synthetic or semisynthetic (cellulosics). †Classified as melt, dry, or wet. ‡60% vinyl and 40% acrylonitrile.

The product resulting from the polymerization reaction of adipic acid and hexamethylene diamine is called nylon 6,6 because each of the raw material chains contain six carbon atoms. Nylon 6 is the homopolymer of caprolactam, and the newly developed aramid fiber, Kevlar, is an aromatic polyamide, poly-*p*-phenylene terephthalamide.

INTERMEDIATES

1. ***Adipic acid.***[2] Adipic acid is prepared by a two-step air oxidation of cyclohexane.



Cyclohexane — Cyclohexanol 50% — Cyclohexanone 40%

[2]Austin, The Industrial Significant Organic Chemicals, *Chem. Eng.* **81** (2) 131 (1974); Danly and Campbell, ECT, 3d ed., vol. 1, 1978, pp. 510–531.

$$\underset{\text{Cyclohexanol}}{C_6H_{11}OH} + \underset{\text{Cyclohexanone}}{C_6H_{11}O} + zHNO_3 \xrightarrow[\substack{100^\circ C \\ 1.03\ MPa}]{\text{cat.}} \underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} + xN_2O + yNO$$

2. ***Hexamethylene diamine.***[3] This compound is made from butadiene or acrylonitrile.

POLYMERIZATION AND FIBER PRODUCTION.[4] The reaction between adipic acid and hexamethylene diamine produces hexamethylene diammonium adipate, commonly called "nylon salt." It is essential that the two intermediates be used in equimolar proportions if high fiber-forming quality polymer is to be produced. Forming the salt assures the correctly balanced proportions. It is also necessary that the material to be polymerized contain very few impurities if high-quality fibers are to be made. This is achieved by recrystallizing the nylon salt before polymerization. Figure 35.2 shows various routes to nylons. The flowchart for nylon yarn, using a batch process, is given in Fig. 35.3.

$$\underset{\text{Adipic acid}}{xHOOC(CH_2)_4COOH} + \underset{\text{Hexamethylene diamine}}{xH_2N(CH_2)_6NH_2} \rightarrow \underset{\text{Hexamethylene diammonium adipate or nylon salt}}{x[H_3N(CH_2)_6NH_3OOC(CH_2)_4COO-]}$$

$$\rightarrow \underset{\text{Poly(hexamethyleneadipamide) or nylon}}{[-HN(CH_2)_6NHOC(CH_2)_4CO-]} + 2xH_2O$$

[3]ECT, 3d ed., vol. 1, 1978, pp. 510–531.

[4]Chapman, *Fibres*, Butterworths, London, 1974.

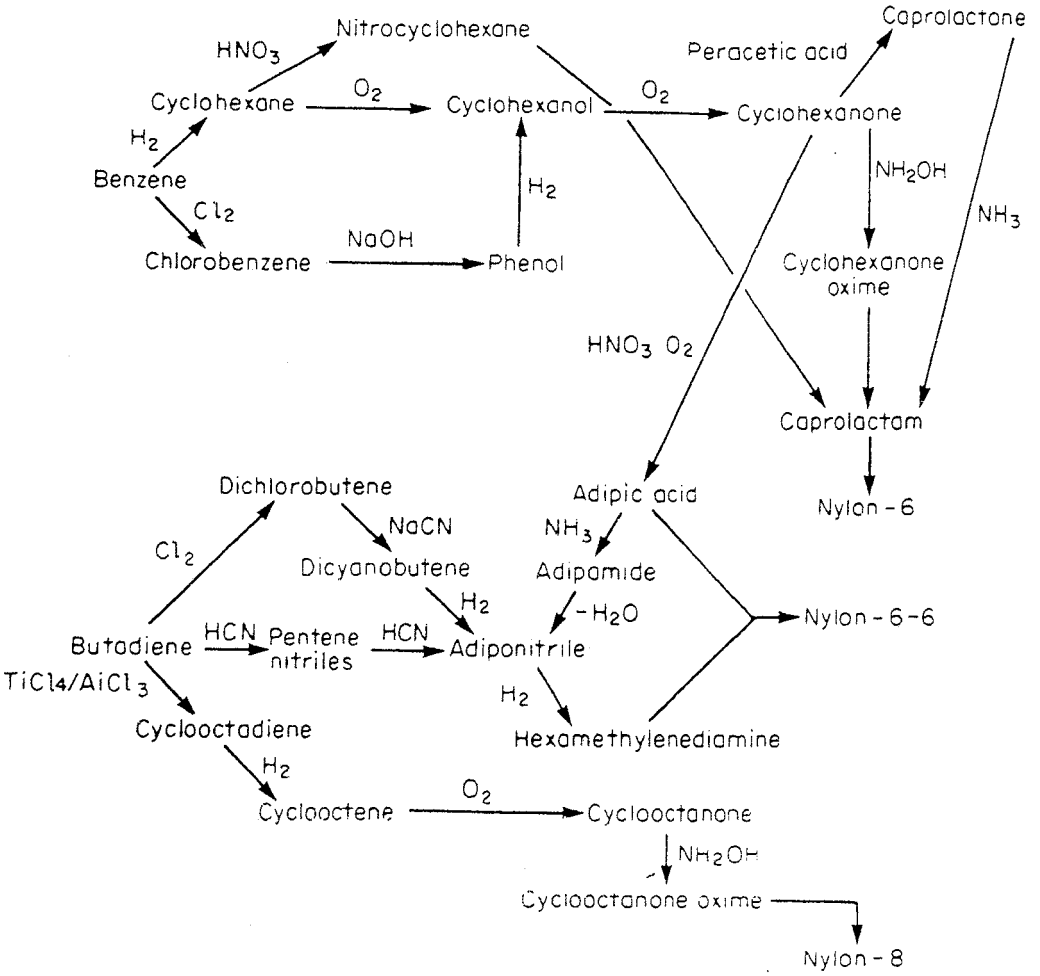


Fig. 35.2. Various routes to nylon. *(Adapted from Marshall Sittig.)*

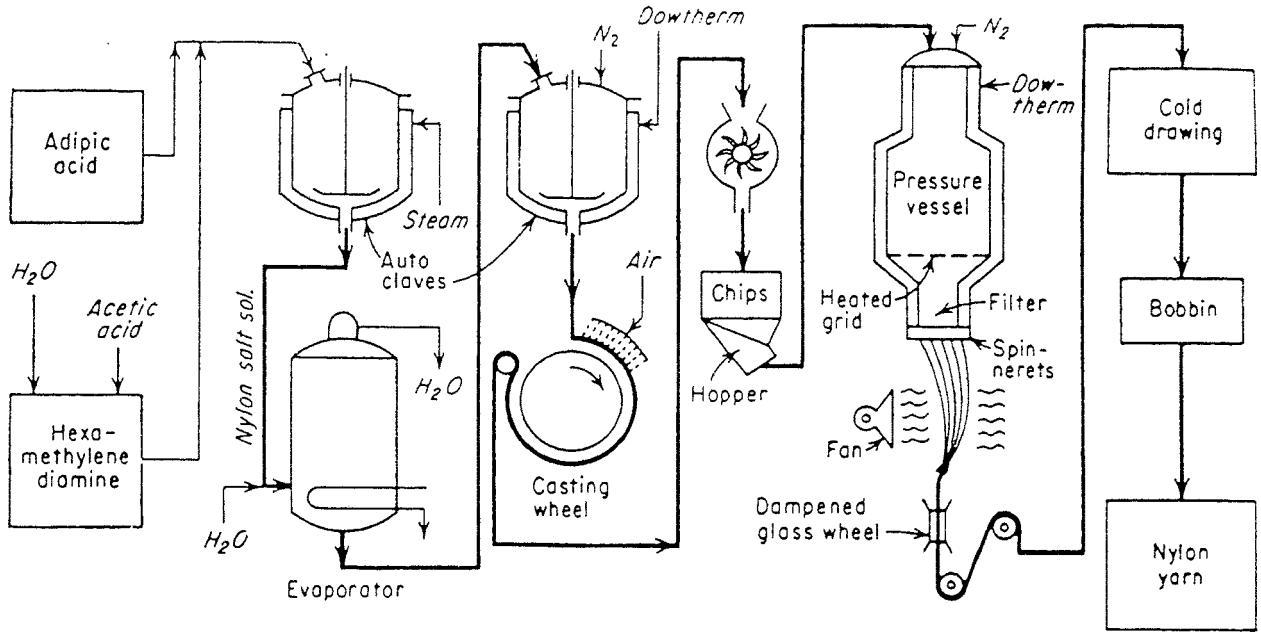


Fig. 35.3. Flowchart for nylon yarn.

The aqueous nylon salt starts on the top level of the factory, and the materials move down by gravity through the various steps. The hexamethylene diammonium adipate solution is pumped to the top level into evaporators and concentrated. Acetic acid is added to the evaporator charge to stabilize the chain length. After evaporation, the salt solution flows into jacketed autoclaves equipped with internal coils and heated by Dowtherm vapor (Fig. 35.4). Here the rest of the water is removed. TiO_2 dispersion is added, and polymerization takes place.

After polymerization is completed, the molten viscous polymer is forced out of the bottom onto a casting wheel by specially purified nitrogen at 175 to 345 kPa. Each 900-kg batch is extruded as rapidly as possible to minimize differences due to thermal treatment of the polymer. A ribbon of polymer about 30 cm wide and 6 mm thick flows on the 1.8-m casting drum. Water sprays on the inside cool and harden the underside of the ribbon; the outer is cooled by air and water. The ribbons are cut into small chips, or flakes, before being blended. Two or more batches are mixed to improve the uniformity of the feed to the spinning machine. The blenders empty into hoppers on a monorail which supply the spinning area.

A typical spinning unit is composed of a metal vessel surrounded by a Dowtherm vapor-heated jacket which keeps the temperature of the vessel above the melting point (263°C) of the nylon. Special precautions are taken to keep the spinning oxygen-free. As the nylon flake enters the vessel it strikes a grid, where it melts and flows through to the melt chamber below. Screw melters, in place of grids, may also be used to melt the flake. The molten polymer passes through the portholes in this chamber to the gear spinning pumps. They deliver it to a sand filter, which is followed by screens and a spinneret plate. The filaments are solidified by air in a cooling chimney and passed in a bundle through a steam-humidifying chamber, where the moisture content is brought to equilibrium in order to stabilize the length of the spun polymer. This is not a problem after stretching or drawing.

After lubrication on a finish roll, the yarn is stretched or drawn to the desired degree by passing it through a differential speed roller system. Here the strength or elasticity characteristics of nylon are developed, because the molecules are oriented from their previous comparatively random oriented arrangement. Stretching may be from three- to sixfold, depending on the mechanical properties desired, being stronger when the orientation by stretching is greatest. The nylon filament is then shipped to various manufacturers for processing.

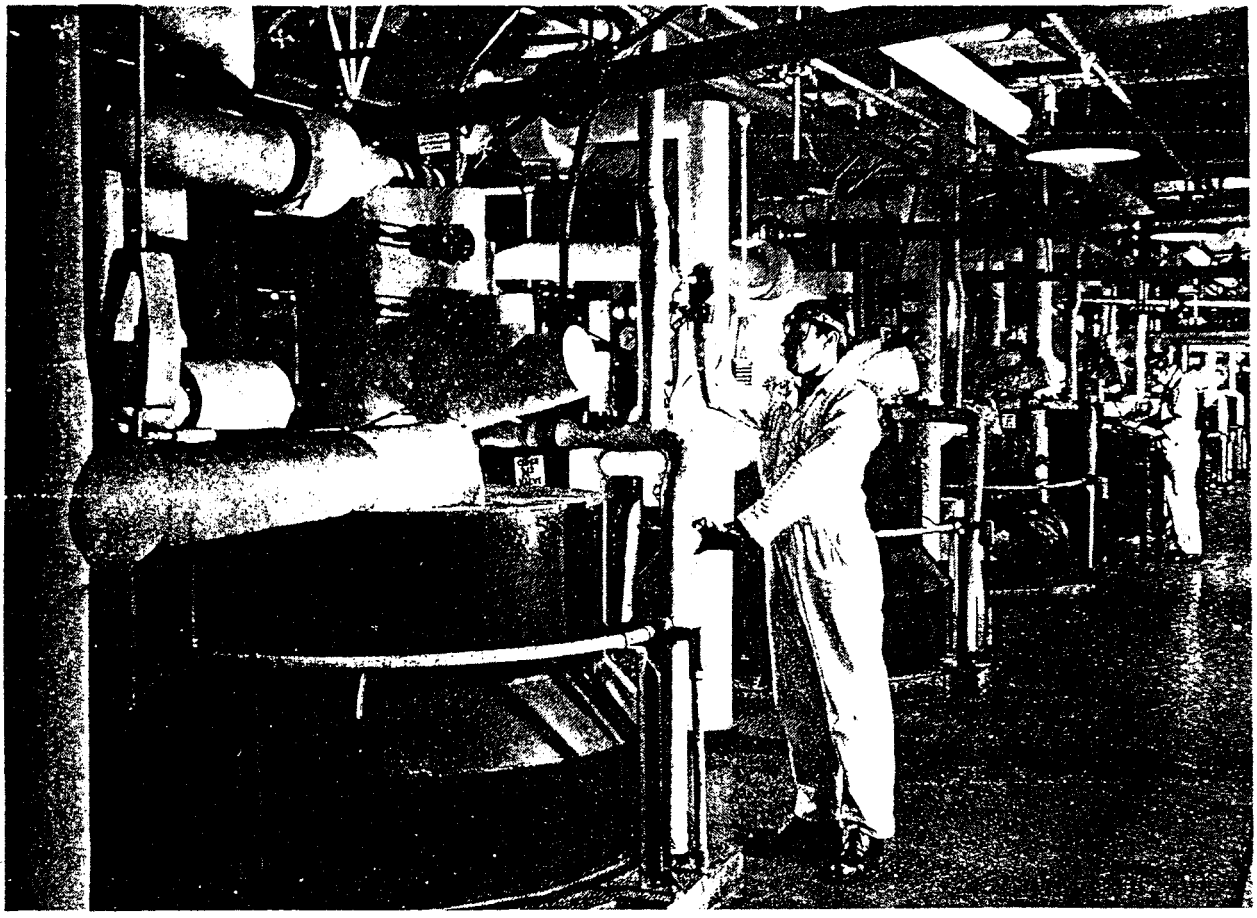


Fig. 35.4. Autoclave in DuPont nylon plant. In these receptacles polymerization takes place to form nylon polymers.

Continuous processing is more economical for larger production items. Here the pressure and temperature of the autoclave cycles are reproduced in a series of pipes and vessels. The continuous process favors uniformity of large-scale product, whereas the batch process favors flexibility among several products.

Like all other synthetic fibers that have become competitively popular, nylon in both the filament and staple form must have certain properties that are superior to natural fibers. It is stronger than *any* natural fiber and has a wet strength of 80 to 90 percent of its dry strength. Its good flexing tenacity makes it very desirable for women's hosiery, and it has good stretch recovery. Nylon's high tenacity has made it important in parachute fabrics and related non-apparel items. Nylon can be dyed by all acid and dispersed dyes. It has a low affinity for direct cotton, sulfur, and vat dyes.

Nylon 6,[5] or nylon caprolactam, is a polymeric fiber derived from only one constituent, caprolactam (Fig. 35.2), $HN\!-\!(CH_2)_5CO$ giving the polymer $[-(CH_2)_5CO-NH-]_n$. It has a lower melting point than nylon 6,6, but it is superior to it in resistance to light degradation, dyeability, elastic recovery, fatigue resistance, and thermal stability. Caprolactam may be made from cyclohexanoneoxime, which is obtained by treating cyclohexanone with hydroxylamine. The more modern process starts with toluene, which is oxidized to benzoic acid,

[5]Moncrieff, *Man-made Fibres*, 6th ed., Wiley, New York, 1975; Chapman, op. cit.

[6]Caprolactam, *Chem. Eng.* **81** (15) 70 (1974); The DSM Phosphate Caprolactam Process, *CHEMTECH* **7** (5) 309 (1977); *Chem. Week* **126** (21) 47 (1980).

hydrogenated to cyclohexane carboxylic acid, and then treated with nitrosyl sulfuric acid to produce caprolactam.[6]

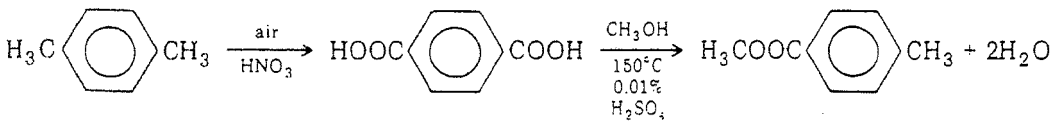
Other nylons have been prepared and have some interesting properties. Copolymers of nylon 6 and nylon 6,6 have improved properties over either polymer alone. These copolymers are used primarily for engineering resins and not for fibers.

Aromatic polyamides (aramids)[7] have at least 85 percent of the amide linkages attached directly to two aromatic rings. The first commercial aramid was Nomex which was prepared by reacting *m*-phenylene diamine with isophthaloyl chloride to produce poly-(*m*-phenyleneisophthalamide). Kevlar is prepared similarly, but it is the para isomer and is produced from *p*-phenylenediamine and terephthaloyl chloride. The meta isomers produce polymers that are heat and flame resistant, and the para isomers produce high strength and high modulus of elasticity. Nomex is used for electrical insulating paper, protective clothing, and in space applications. Kevlar possesses ultrahigh strength and is used as a tire cord. When it is produced as a very short fiber, called Kevlar Pulp, it is used as a replacement for asbestos.

Polyesters

The common polyester fibers are polymers of the ester formed from dimethyl terephthalate and ethylene glycol.

INTERMEDIATES. Dimethyl terephthalate[8] is prepared by oxidation of *p*-xylene and subsequent esterification with methyl alcohol.



p-xylene — Terephthalic acid — Dimethyl terephthalate

POLYMERIZATION AND FIBER PRODUCTION. Polymerization is a two-stage process in which the monomer is first prepared either by an ester interchange between dimethyl terephthalate and ethylene glycol, or by direct esterification of terephthalic acid.

$$p\text{-}H_3COOCC_6H_4COOCH_3 + 2CH_2OH\cdot CH_2OH \rightarrow$$

$$p\text{-}HOCH_2CH_2OOCC_6H_4COOCH_2CH_2OH + 2CH_3OH$$

Ester monomer

$$p\text{-}HOOCC_6H_4COOH + 2CH_2OH\cdot CH_2OH \rightarrow$$
$$p\text{-}HOCH_2CH_2OOCC_6H_4COOCH_2CH_2OH + 2H_2O$$

Ester monomer

The second stage is the polymerization of the monomer

$$n(\text{monomer ester}) \xrightarrow{260^\circ C} (n-1)HOCH_2CH_2OH + H-[OCH_2CH_2OOCC_6H_4CO]_n-OCH_2CH_2OH$$

Polyethylene terephthalate

[7]ECT, 3d ed., vol. 3, 1978, p. 213; *Chem. Week* 127 (22) 20 (1980); *Chem. Week* 132 (8) 43 (1983).

[8]Austin, *Chem. Eng.* 81 (22) 114 (1974).

The polymer is extruded from the bottom of the polymerizer through a slot or holes on to the surface of a water-cooled drum. The ribbon is cut to chips and dried before melt spinning in a manner similar to that described for nylon. The polymer chain contains approximately 80 benzene rings. Figure 35.5 shows the flowchart for the entire process. The filaments are stretched, with the application of heat, to about three to six times their original length.

Table 35.2 shows some of the properties of polyester fiber. It is particularly well suited for blending with wool and cotton to yield good esthetics in woven fabrics, such as men's summer suits, men's shirts, and women's dresses and blouses, and is used alone in knitted fabrics and some woven fabrics. Because of its strength it is important in the tire-cord and cordage fields, it is also used for sewing thread, fire hose, and V-belts. It is not used for women's stockings because its elastic modulus is too high, and thus it does not recover rapidly after stretching. In staple form it is employed as stuffing for pillows, sleeping bags, and comforters. Its production in 1981 was almost 1.9×10^6 t.

Acrylics and Modacrylics

Polyacrylonitrile $(-CH_2CHCN-)_n$ is the major component of several industrial textile fibers, but DuPont's Orlon was the first to attain commercial-scale operation. Dyeable acrylics are generally copolymers with modifying constituents.

Orlon is made by polymerizing acrylonitrile. The ivory-white polymer is dissolved in an organic solvent, generally dimethylformamide, although it can be dissolved in many concentrated solutions of salts, like lithium bromide or more successfully in other organic solvents.

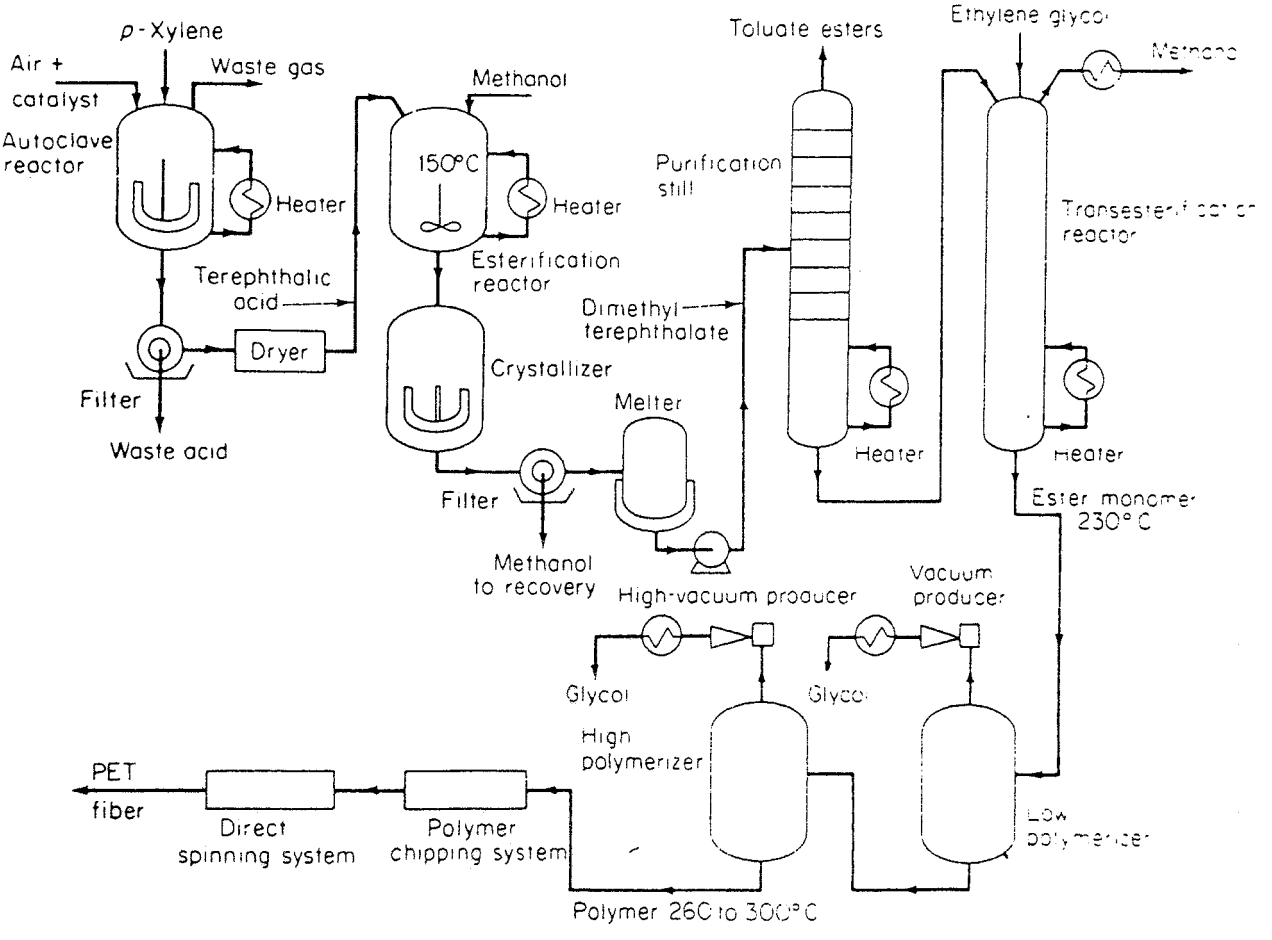


Fig. 35.5. Flowchart for the manufacture of polyester fibers.

Table 35.2 Comparison of Selected Synthetic Fibers

Fiber	Wool	Acrylic	Modacrylic	Polyesters	Nylon
Tensile strength, g/denier	1.0–1.7	4.0–5.0	3.0	4.4–6.6	4.7–5.6
Elongation, %	25–35	16–21	16	18–22	25–28
Elastic recovery	0.99 at 2%	0.97 at 2%	0.80 at 2%	90–110 at 4%	100 at 8%
Strength, mPa	137–200	405–508	302–453	536–797	467–556
Stiffness, g/denier*	3.9	24	30	23–63	20
Abrasion resistance†	90	330		1570	2520
Water absorbency‡	21.9% at 90 RH	2% at 95 RH	—	0.5% at 95 RH	8% at 95 RH
Effect of heat	Becomes harsh 100°C, decomposes at 130°C	Sticking point 235°C	Sticking point 235°C	Sticking point 240°C	Melts 263°C
Effect of age	Little	Little	Little	Little	Slight
Effect of sun	Weakened	Very resistant	Slight	Little	Weakened
Effect of acids (concentrated, room temp.)	Resistant	Resistant	Resistant	Resistant	Weakened
Effect of alkalies	Susceptible	Partly resistant	Resistant	Resistant	Resistant
Effect of organic solvents	Resistant	Resistant	Resistant	Resistant	Resistant
Dyeability	Good	Good	Good	Difficult	Good
Resistance to moths	None	Wholly	Wholly	Wholly	Wholly
Resistance to mildew	Good	Wholly	Wholly	Wholly	Wholly

*Crease resistance. †Wet flex test, number of flexes. ‡RH, Relative humidity. SOURCES Wool vs. Synthetics, *Chem. Week* **69** (3) 11 (1951); Moncrief, *Man-Made Fibers*, 6th ed., Wiley, New York, 1975.

such as dimethoxyacetamide and tetramethylene cyclic sulfone. The solution is filtered and then dry-spun, utilizing the same spinning technique long used for acetate, namely, in solution through spinnerets, with the solvent evaporated to furnish the dry fiber. Unlike nylon which is drawn at room temperature, acrylics, like polyester, are drawn at elevated temperatures in a special machine. The fibers are stretched to three to eight times their original length to orient the molecules into long parallel chains for final strength. The staple fiber has esthetic properties like those of wool. The acrylics' resistance to chemical attack, and especially to weathering, makes them highly useful in several fields. Other acrylics, like Acrilan and Creslan, are spun wet into a coagulating bath. The end uses for acrylic fibers comprise sweaters, women's coats, men's winter suiting, carpets, and blankets. Blends with wool and other synthetics are common in some end uses. Acrylics are also suitable for pile fabrics and filter cloth.

MODACRYLIC FIBERS (MODIFIED ACRYLICS). This is a generic name for synthetic fibers in which the fiber-forming substance is any long-chain synthetic polymer composed of less than 85% but at least 35% by weight of acrylonitrile units (Federal Trade Commission).

Dynel is the name given by Union Carbide to their staple copolymer modacrylic fiber made from a resin of 40% acrylonitrile and 60% vinyl chloride. The resin is converted into staple in a continuous wet-spinning process (cf. viscose rayon). The white resin powder is dissolved in acetone, filtered, and run through a spinneret, where the fibers are formed in an aqueous spinning bath. The fiber is dried, cut, and crimped. Dynel is similar to wool in many respects and has some superior characteristics. It is used for work clothing, water-softener bags, dye nets, filter cloth, blankets, draperies, sweaters, pile fabrics, etc.

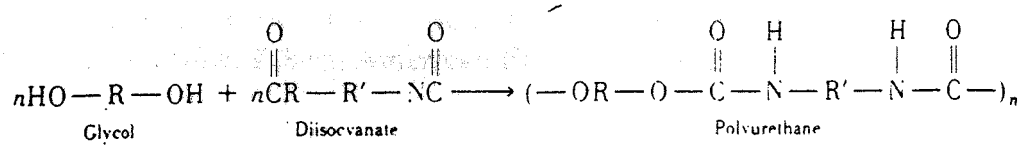
Vinyls and Vinylidines

Saran is the copolymer of vinyl chloride and vinylidene chloride. It is prepared by mixing the two monomers with a catalyst and heating. Color is added by introducing pigment into the mass. The copolymer is heated, extruded at 180°C, air-cooled, and stretched. Saran is resistant to mildew, bacterial, and insect attack, which makes it suitable for insect screens. Its chemical resistance makes it advantageous for filter-cloth applications; however, its widest use has been for automobile seat covers and home upholstery. Much film is made from Saran.

Vinyon is the trade name given to copolymers of 90% vinyl chloride and 10% vinyl acetate. The copolymer is dissolved in acetone to 22% solids and filtered, and the fibers are extruded by the dry-spinning technique. After standing, the fibers are wet-twisted and stretched. Resistance to acids and alkalies, sunlight, and aging makes Vinyon useful in heat-sealing fabrics, work clothing, filter cloths, and other related applications.

Spandex

Spandex, a generic name, is defined by the Federal Trade Commission as "a manufactured fiber in which the fiber-forming substance is a long chain synthetic polymer comprising at least 85% of a segmented polyurethane." Trade examples of these are Lycra, Glospan, and Numa fibers. Lycra, DuPont's spandex fiber, results from the following reaction:



The segmented polyurethane structure is achieved by reacting diisocyanates with long chain glycols which are usually polyesters or polyethers of 1000 to 2000 molecular weight range. The product is then chain-extended or coupled through the use of glycol, a diamine, or perhaps water. This gives the final polymer, which is converted into fibers by dry spinning. In the finished fiber the chains are randomly oriented and, when stretched, the chains become oriented but exhibit spontaneous recovery to the disordered state upon release of the force. This fiber is used in foundation garments, hose, swimwear, surgical hose, and other elastic products, sometimes in conjunction with other fibers, such as acrylic, polyester, acetate, rayon, or natural fibers, which are wrapped around a core of the elastic spandex fiber.

Polyolefins

Polyolefin fibers are usually made of polyethylene and polypropylene. They excel in special cases, such as ropes, laundry nets, carpets, blankets, and backing for tufted carpets, but are difficult to dye and their melting point is low. In 1981 the annual consumption in the United States was 292,000 t. See Chap. 34 for the preparation of the polymer.

The polymer is spun from a melt at about 100°C above the melting point because the viscosity of the molten polymer at or near the melting point is very high.

Fluorocarbons

Teflon is polytetrafluoroethylene $[-(C_2F_4)-_n]$ (Chap. 20) and as fiber or film is nonflammable and highly resistant to oxidation and the action of chemicals, including strong acids, alkalies, and oxidizing agents. It retains these useful properties at high temperatures (230 to 290°C) and is strong and tough. A very important property is its low friction, leading, with its chemical inertness, to wide use in pump packings and shaft bearings.

Glass Fibers

Fiberglass wearing materials were prepared as early as 1893, when a dress of fibers about five times the diameter of the present-day product was made by Owens. Since that time, however, numerous improvements have been discovered, until at present continuous fibers as small as 5 μm in diameter are possible. The largest and original (1938) manufacturer of glass fibers is the Owens-Corning Fiberglas Corp., which markets its product under the trade name Fiberglas. Production of textile fibers in 1981 was 472,000 t. Glass fibers are derived by two fundamental spinning processes: blowing (glass wool) and drawing (glass textile fiber), as outlined in Fig. 35.6. Textile fibers[9] can be made as continuous filaments or staple fibers and are manufactured from borosilicate glasses composed of 55% silica, and substantial amounts of alumina, alkaline earths for fluxing, and borates (Table 35.3). The low strong-alkali level reduces susceptibility to corrosion. Glass for textiles must be equal in purity to the better grades of optical glass and, when molten, must be free of any seeds or bubbles that would tend to break the continuity of the fiber.

In the continuous-filament process, specially prepared and inspected glass marbles are melted, or a batch of highly purified molten glass is allowed to flow through a set of small

[9]Carpet of Glass, *Text. Ind.* 139 (1) 40 (1975); Lowenstein, *The Manufacturing Technology of Continuous Glass Fibers*, American Elsevier, New York, 1973.

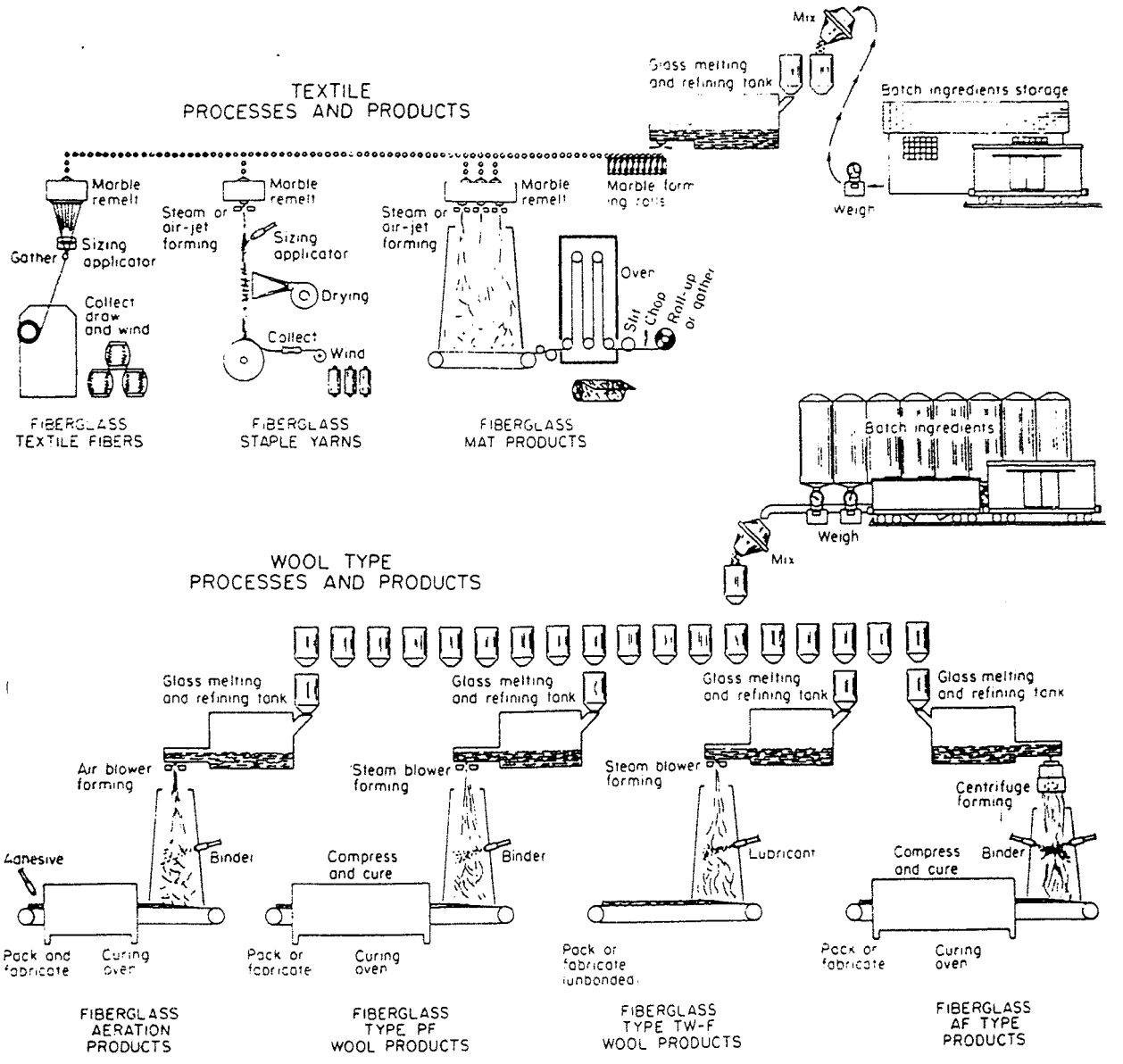


Fig. 35.6. Flowchart for Fiberglas production. *(Owens-Corning Fiberglas Corp.)*

holes (usually 102 or 204 in number) in a heated platinum bushing at the bottom of the furnace. The fibers are led through an "eye" and then gathered, lubricated, and put on high-speed winders, which rotate so much faster than the flow from the bushing that the filaments are drawn down to controlled diameters. The fibers are used for electrical insulation in motors and generators, structural reinforcement for plastics, fireproof wall coverings, and tire cords.[10]

In the production of staple fiber, glass is automatically fed at regular intervals to a small

[10]Rolston, Fiberglass Composite and Fabrication, *Chem. Eng.* 87 (2) 96 (1980); A Code to Build Trust in FRP Equipment, *Chem. Eng.* 86 (13) 78 (1979).

Table 35.3 Basic Ingredients for Continuous-Filament Glass Fiber (in percent)

Silicon dioxide	52–56	Boron oxide	8–13
Calcium oxide	16–25	Sodium and potassium oxides	0–1
Aluminum oxide	12–16	Magnesium oxide	0–6

electrically heated furnace. The molten glass discharges continuously through a spinneret. Directly below the orifice plate is a jet discharging high-pressure air or steam in such a manner as to seize the molten filaments and drag them downward, decreasing their diameter. The individual fibers are projected through the path of a lubricating spray and a drying torch onto a revolving drum. The resulting web of fibers on the drum is drawn off through guides and wound on tubes, and, after drafting and twisting to form yarns, sent to weaving and textile fabrication. A new process treats the fabrics at high temperature to relax the fibers, thereby increasing the drapability and "hand" and removing all sizing from the yarns to make them receptive to finishing materials. Coloring can be achieved by the use of resin-bonded pigments applied during finishing. End-use applications include curtains and draperies.

In the manufacture of glass wool for thermal and acoustical insulation, borosilicate glasses composed of approximately 65 and 35% fluxing oxides and borates, respectively, are melted in large regenerative furnaces. In blowing, molten glass at 1500°C flows through the small holes of a platinum alloy plate called a bushing, or from a centrifuge, at one end of a standard glass furnace. The melt streams are caught by high-speed gaseous jets and pulled out into fibers that are hurled onto a moving belt. This wooly mass is impregnated with various binders and formed into many shapes for use as insulation, or set into frames for use as air filters. Glass-fiber mats and wool have now largely superseded rock wool for insulation.

Multicomponent Fibers

Multicomponent fibers[11] have been prepared which possess superior properties to either component if spun alone. These fibers are prepared by spinning two or more polymeric compounds together. These compounds may be variants of the same polymer, as two different polymers of polypropylene, or two or more chemically unrelated materials, such as polyamides and polyesters. The choice of the starting materials is determined by the properties desired in the finished fiber. These properties may be better dyeability, permanent crimp, or silklike feel, etc.

CELLULOSIC FIBERS

Rayon and Acetate

USES AND ECONOMICS. In 1981 the U.S. production of rayon and acetate was as shown in Fig. 35.1 and amounted to 349,000 t. High tenacity viscose yarn is used mainly in cords for tires, hose, and belting. The difference in strength between ordinary and high tenacity viscose depends on the amount of orientation[12] imparted to the fiber molecules when they are made. The hydroxyl groups in the cellulose molecules enable the fiber to absorb water, resulting in low wet strength. Hydroxyl groups also serve as sites for hydrogen bonding, and thus in the dry state, serve to hold molecules together despite strong bending, resulting in fibers which tend to maintain their dry strength well even at high temperatures. The price of rayon and

[11]Placek, *Multicomponent Fibers*, Noyes, Park Ridge, N.J., 1971.

[12]Molecules lined up in one direction by stretching during spinning and drawing.

acetate varies according to the size of the filaments, process of manufacture, and type of finish. Textile rayon and acetate are used primarily in women's apparel, draperies, upholstery, and blends with wool in carpets and rugs. In 1981 cotton, wool, and silk accounted for 55 percent of the fibers produced worldwide. It has been predicted that by 1985 new, improved rayons will take over a large part of cotton's market because of increases in the price of cotton, shift of land devoted to growing cotton to growing food, and, in the United States, the large expenditures that mill owners must make to comply with the stringent government cotton dust regulations.

RAW MATERIALS. The viscose process is based on sulfite, and a little sulfate wood pulp. If sheet cellulose, the form used in viscose manufacture, is desired, the sulfate pulp, after the bleaching treatment has been completed, is blended with several other batches, passed successively through a beater and a refiner (see manufacture of pulp for paper in Chap. 33), and formed into sheets on a Fourdrinier.[13] Viscose rayon is a major consumer of sulfuric acid, caustic soda, and carbon disulfide. Titanium dioxide is added to deluster the yarn. Cellulose acetate employs large quantities of acetic anhydride, glacial acetic acid, sulfuric acid, and acetone to swell the wood pulp. In addition to this important consumption of basic chemicals, the fiber industry needs significant quantities of dyes and other chemicals.

The viscose process produces filaments of regenerated cellulose, and the acetate forms a thread that is a definite chemical compound of cellulose, cellulose actate. Although each of these processes is quite different as far as details of procedure are concerned, they all follow the same general outline: solution of the cellulose through a chemical reaction, ageing or ripening of the solution (peculiar to viscose), filtration and removal of air, spinning of the fiber, combining the filaments into yarn, purifying the yarn (not necessary for acetate), and finishing (bleaching, washing, oiling, and drying).

REACTIONS[14]

$$(C_6H_9O_4\cdot OH)_x + xNaOH \longrightarrow (C_6H_9O_4\cdot ONa)_x + xH_2O$$

Cellulose — Alkali cellulose

$$(C_6H_9O_4\cdot ONa)_x + xCS_2 \longrightarrow \left(C_6H_9O_4-O-C(=S)-SNa\right)_x$$

Cellulose xanthate

$$3\left(C_6H_9O_4-O-C(=S)-SNa\right)_x + 2xH_2O \longrightarrow \left(C_{18}H_{27}O_{12}(OH)_2O-C(=S)-SNa\right)_x - 2xCS_2 + 2xNaOH$$

Opened xanthate

$$\left(C_{18}H_{27}O_{12}(OH)_2O-C(=S)-SNa\right)_x + \frac{x}{2}H_2SO_4 \longrightarrow (C_6H_9O_4\cdot OH)_x + xCS_2 + \frac{x}{2}Na_2SO_4$$

Viscose rayon

[13]*Chem. Week* 129 (5) 25 (1981); *Textile Ind.* 146 (6) 60 (1982); Layman, Rayon Aims for Specialty Niches in Low-Growth Market, *Chem. Eng. News* 61 (8) 10 (1983).

[14]The cellulose molecule is composed of a large, undetermined number of glucose units, here represented as $(C_6H_9O_4OH)_x$. The value of x does not remain constant throughout these reactions. Each reaction causes a reduction in the molecular weight of the cellulose molecule, so that the viscose-rayon molecule is considerably smaller than the cellulose originally fed in. Some CS_2 breaks away from the cellulose xanthate during the ripening process.

Cellulose acetate

$$\underset{\text{Cellulose}}{[C_6H_7O_2\cdot(OH)_3]_x} + 3x(CH_3CO)_2O \longrightarrow \underset{\text{Cellulose acetate}}{[C_6H_7O_2(O_2CCH_3)_3]_x} + 3xCH_3CO_2H$$

VISCOSE MANUFACTURING.[15] The finished filament is pure cellulose, as shown by the equations, but, because it consists of smaller molecules than the cellulose of the original wood pulp or cotton, it possesses different physical properties.

The process as shown in Fig. 35.7 can be broken down into the following sequences:

The cellulosic raw material (sheets made from sulfite or sulfate pulp) is charged to a steeping press containing vertical perforated steel plates and is steeped either batchwise or continuously in a caustic soda solution (17 to 20%) for about 1 h at 13 to 17°C to dissolve the cellulose.

The excess liquor is drained off, removing impurities such as cellulose degradation products. The soft sheets of alkali cellulose are reduced to small crumbs in a shredder. This requires 2 to 3 h, and the temperature is maintained at 18 to 20°C.

[15]ECT, 3d ed., vol. 19, 1982, p. 855; Chapman, op. cit.

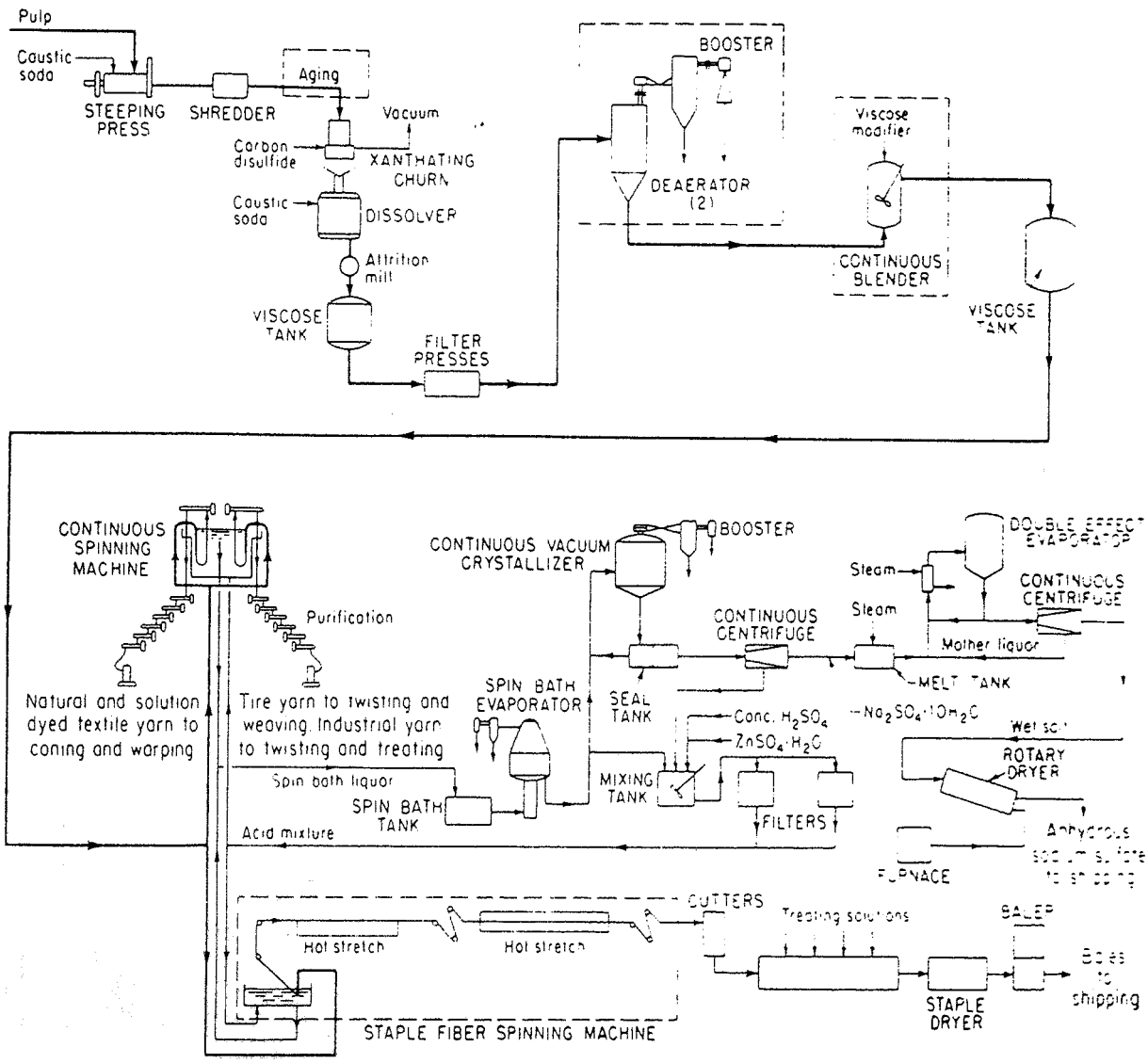


Fig. 35.7. Flowchart for viscose rayon production. [*Chem. Eng.* 71 *(14) 110 (1964)*]

The crumbs of alkali cellulose are aged either batchwise or continuously for 24 to 48 h at 24°C in large steel cans. Some oxidation and degradation occur, although the actual chemical change is unknown. Physically, correct aging produces a solution of suitable viscosity for spinning after xanthation.

The aged crumbs are dropped into large, cylindrical xanthating churns. Carbon disulfide weighing between 30 to 40% of the dry recoverable cellulose is slowly added under carefully controlled temperature and reduced pressure during 2 h of churning, during which time the crumbs gradually turn yellow and finally deep orange, and coagulate into small balls.

Still in batch form, the cellulose xanthate balls are dropped into a jacketed dissolver (vis-solver) containing dilute sodium hydroxide. The xanthate particles dissolve in the caustic, and the final product, viscose solution, contains 6 to 8% cellulose xanthate and 6 to 7% sodium hydroxide. This reaction takes 2 to 3 h. If desired, delustering agents, such as titanium dioxide or organic pigments, are added to the viscose solution in the mixer. The result is a viscous, golden-brown liquid. The remainder of the process (Fig. 35.7) through ripening and spinning is continuous. DuPont has developed a continuous belt xanthation process[16] that is claimed to cut costs and produce a higher quality product. The vessel used is completely enclosed which cuts carbon disulfide losses.

During the ripening the proportion of combined sulfur decreases and the ease of coagulation increases. Thirty years ago, this conversion took 4 to 5 days, but now improved technology has reduced it to about 24 h. In a series of tanks (only one is shown in Fig. 35.7) the reaction proceeds under deaeration and continuous blending with modifiers (viscose additives, mainly amines and ethylene oxide polymers) that control neutralization and regeneration rates.

Finally, in two continuous vacuum-flash boiling deaerators (at high vacuum and below room temperature), small air bubbles are removed that would either weaken the final yarn or cause breaks during spinning.

In spinning, viscose is forced by gear pumps through thimble-like spinnerets of noble metal, each with from 750 to 2000 holes. The fine streams thus formed are injected into the spin bath where they coagulate and the cellulose is regenerated to form fiber. Sulfuric acid in the

[16]How to Make Viscose Rayon Continuously, Chem. Week. **129** (5) 25 (1981)

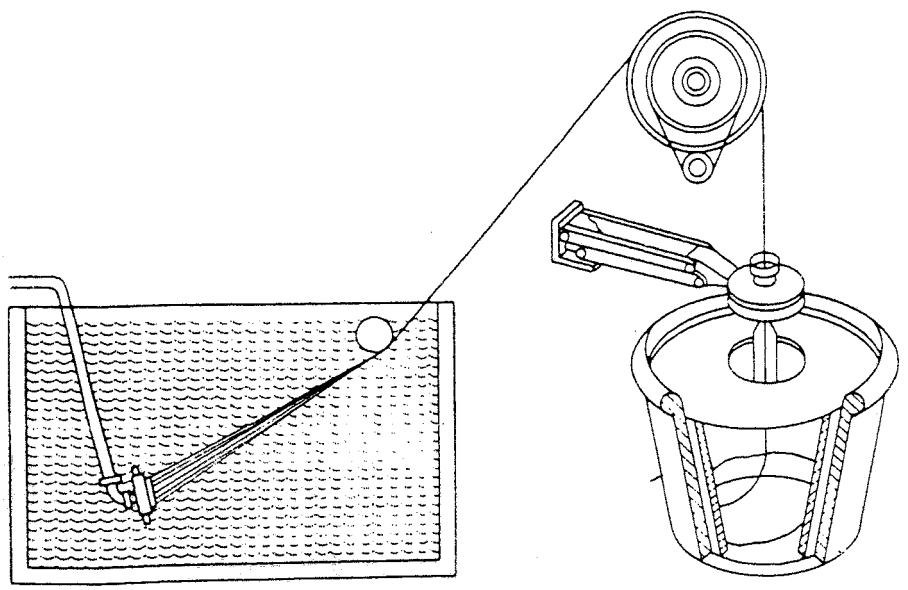


Fig. 35.8. Spinning in the viscose process.

spinning bath neutralizes free NaOH and decomposes xanthate and various viscous by-products containing sulfur, thus liberating CS_2, H_2S, CO_2, and S. Salts such as $ZnSO_4$ and Na_2SO_4 coagulate the xanthate, forming relatively stable metal complexes. The sulfuric acid/salts ratio is a key control point, which, although coagulation and regeneration take place together, ensures that the xanthate gels before the acid can attack and decompose it. Four percent or more glucose prevents crystallization of salts in the filaments.

Three separate continuous spinning and treating procedures are outlined in Fig. 35.7.

1. Textile yarns are twisted into continuous yarn as the filaments leave the spinneret. They are dyed (then or later) and sent to coning and warping.
2. Tire yarns are stretched to impart strength over a series of thread-advancing rolls where wash and other treatments are applied, such as deacidifying, desulfurizing, and bleaching.
3. Staple yarns are spun on the machine in the lower part of Fig. 35.7 by combining filaments from many spinnerets without twisting and cutting them into uniform lengths. Each year more viscose filaments are made into staple fiber.

The actual process of continuous spinning has reduced the elapsed time from hours to minutes. The types of machines in general use are continuous, bucket, and bobbin. Three-quarters of U.S. production is from the long-used bucket type (Fig. 35.8). If a bucket machine is used, the spinneret head dips horizontally into the spinning solution, and several of the filaments are gathered into a thread and fed down to a small centrifugal bucket spinning at about 7500 rpm. The bucket imparts one twist to the filaments per revolution and removes a greater portion of the occluded bath liquor through perforations in the periphery.

If a bobbin machine is used, the spinnerets point vertically upward into the spinning bath, and the filaments are wound on a revolving bobbin. No twist is imparted to the thread.

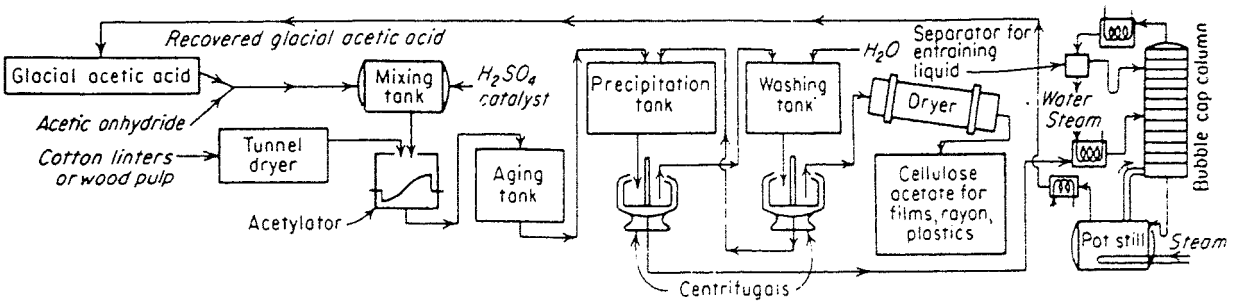
Yarn from either type is washed to remove the spinning liquor and desulfurized by treating with a 1% sodium sulfide solution. They are then washed in hypochlorite solution, washed again in water, dried, and coned.

Originally rayon filaments had a cylindrical cross section and a silky appearance and feel. In an effort to produce a rayon that is more like cotton, the shape of the fiber has been modified. Avril III and Avril-Prima are highly crimped, very high wet modulus fibers that have irregularly shaped cross sections and have many cottonlike properties.[17]

CELLULOSE ACETATE MANUFACTURE. Cellulose acetate and its homologs are esters of cellulose and are not regenerated cellulose. The raw material for the spinning solution is prepared by charging acetic anhydride, glacial acetic acid, and a small quantity of sulfuric acid as a catalyst to a jacketed, glass-lined, agitated, cast-iron acetylator (see Fig. 35.9). The mixture is cooled to 7°C, and the wood pulp is added slowly. The acetylation requires 5 to 8 h, and the temperature is maintained below 50°C. The viscous fluid is diluted with equal parts of concentrated acetic acid and 10% sulfuric acid and allowed to age for 15 h at 38°C. Hydration of some of the acetate groups occurs. No method has been devised whereby cellulose can be converted directly to a product of the desired acetyl content. It is necessary to transform it first to the triacetate and partly hydrolyze off the required proportion of acetate groups. The desired material is usually about half way between triacetate and diacetate.

The hydration is stopped by running the mixture into a large volume of water and precipitating the secondary acetate. The secondary acetate is centrifuged to separate it from the still strong acetic acid which is recovered, concentrated, and used over.

[17] A Rayon Rebirth, *Chem. Eng.* 86 (7) 113 (1979).



In order to produce 1 kg of acetate rayon the following materials and utilities are required.

Pulp	0.70 kg	Sulfuric acid	0.1 kg
Acetic anhydride	0.2 kg	Direct labor	0.09 work-h
Acetic acid	3.25 kg	Acetone loss	0.2 kg

Fig. 35.9. Flowchart for cellulose acetate manufacture.

The flakes are washed several times by decantation and are then ready to be used in preparing the spinning solution by dissolving the dry flakes in acetone in a closed, agitated mixer. If desired, a delustering pigment is added. Several batches are blended, filtered, and sent to the spinning machine. The solution is forced through spinnerets into a current of warm, moist air. The acetone evaporates and is recovered, leaving a filament of cellulose acetate.

These filaments are twisted and coned in the same manner as those of the previously described rayons. Some yarns are sold without a twist. Filament yarn is made by twisting the threads before winding on the bobbin. Tow consists of threads gathered without twisting and is cut into short lengths for use as staple fibers.

The economical operation of the process depends on the recovery of as many of the chemicals as possible. For every kilogram of cellulose acetate about 4 kg of 30 to 35% aqueous acetic acid is obtained. Dilute acetic acid from various parts of the process is run through a thickener to remove the last traces of cellulose acetate and then concentrated in a distilling unit and reconverted to acetic anhydride. The acetone-laden air from the spinning machines may be passed through activated charcoal to absorb the solvent (which is subsequently recovered by steaming and rectification) or by cooling the air in water towers and simultaneously dissolving out the acetone, the water-acetone mixture later being rectified. Liquid absorption and distillation are also employed.

Cellulose triacetate fiber, Arnel, is made by Celanese Corp. It is reported to possess resistance to glazing at high ironing temperatures, complete machine washability, low shrinkage in stretching, good crease and pleat retention, and an adaptability to a wide range of colors, designs, and prints.[18] It is prepared by dissolving the triacetate in dichloromethane instead of acetone as is used for the diacetate.

CARBON FIBERS[19]

High-modulus carbon fibers are prepared from rayon, polyacrylonitrile (PAN), or pitch. Rayon fibers are charred at 200 to 350°C and then carbonized at 1000 to 2000°C. The result-

[18]Moncrieff, op. cit.

[19]ECT, 3d ed., vol. 4, 1978, p. 622; Delmonte, *Technology of Carbon and Graphite Fiber*

ing carbon fibers are then heat treated at 3000°C and stretched during the heat treatment. This is a very costly process as the overall yields are only about 25 percent. These rayon-produced fibers are used for manufacturing heat shields for aerospace vehicles, and for aircraft brakes.

Fibers can be produced from PAN in a better yield, but the Young's modulus is not as high as those prepared from rayon. The PAN is stretched 100 to 500 percent at 100°C, heated at 190 to 280°C for 0.5 to 5 h, and then carbonized at 1000 to 1300°C. The yield is about 45 percent. The modulus can be increased by heating above 2500°C.

Coal tar or petroleum pitch is first heated to form a liquid crystal state (mesophase). Yarn is spun from the liquid and thermoset in an oxygen atmosphere. When heated to 3000°C the fibers have a high modulus and require no costly stretching.[20]

Carbon fibers are sold in three forms:

1. ***Low modulus (138 GPa) mat.*** This is used as an electrically conducting surface for electrostatic spraying and in injection molding to get electrical conductivity, resistance to heat, and improved wear (for bearings).
2. ***Medium modulus (138-517 GPa).*** This fiber can be formed into fabrics.
3. ***High modulus (above 345 GPa).*** This is the lowest priced high-modulus yarn available and is used when stiffness is critical.

Carbon fibers are used for reinforcing plastics which can be used for sporting goods (fishing rods, etc.) and engineering plastics.

FINISHING AND DYEING OF TEXTILES

Many of the textile industries mill operations abound in chemical engineering problems. Dyeing, bleaching, printing, special finishing (such as for crease recovery, dimensional stability, resistance to microbial attack and ultraviolet light), flame resistance, scouring, water treatment, and waste disposal are examples of mill treatments where unit operations as filtering, heating, cooling, evaporation, and mixing are involved.

The modification[21] of fibers and fabrics by special treatments to change their properties and to improve their usefulness is increasing. Three important finishes consist of flameproofing or fire retarding, mildew or rotproofing, and water repellency. Temporary flame proofing of cellulosic fibers is achieved by the application of ammonium salts or borax and boric acid. Ideal fabric flame proofing, which allows cleaning or laundering and yet maintains desirable fabric characteristics is difficult, although much research is directed toward this aim,[22] and some processes are finding commercial acceptance. Mildew proofing of cellulosic fabrics may be obtained by the use of many organic and inorganic compounds. Commonly used materials include acrylonitrile, chlorinated phenols, salicylanilide, and organic mercurial compounds. copper ammonium fluoride, and copper ammonium carbonate. To produce water-repellent finishes durable to the usual cleaning processes, special quaternary ammonium compounds are heat-treated onto the fiber. Shrink proofing of wool employs various chlorinating processes, especially for socks, shirts, knitting yarns, and blankets. Another method for shrink

[20]Barr et al., High Modulus Carbon Fibers from Pitch Precursor, New and Specialty Fibers. Applied Polymer Symposia No. 29, ACS, Columbus, Ohio, 1975.

[21]For Fibers, Finish Is Just the Start, *Text. World* 129 (7) 341 (1979).

[22]See Chap. 16.

proofing woven fabrics is to coat them with a melamine-formaldehyde product. Thermosetting resins are being widely used to impart crease or wrinkle resistance to cellulosic fibers. Commonly used products include urea-formaldehyde and melamine-formaldehyde resins. The fabric is treated with water-soluble precondensates, together with a condensation catalyst. The treated fabric is dried and heated at an elevated temperature to set the resin within the fiber structure. Many other special treatments for fabrics include mothproofing, improving of resiliency, stiffening, softening, eliminating electrostatic charge during processing, sizing, lubricating, and inhibiting atmospheric gas fading of dyes. In recent years chemical finishes have been used to react with the fiber material, e.g., cotton, and thereby to change its properties by esterification (carboxymethylation) or amination (2-aminosulfuric acid).

FILMS[23]

The first successful plastic film was cellulose nitrate. This was soon followed by regenerated cellulose and cellulose acetate. Up until 1950 regenerated cellulose film had the largest share of the market. The advent of polyethylene was the first to challenge cellulose's supremacy. Now films are produced from other polyolefins, polyvinyl chloride and acetate, polystyrene and polystyrene copolymers, and polyamides, polycarbonates, acrylics, and many other polymers.

VISCOSE AND CELLULOSE ACETATE. Transparent viscose film (Cellophane) is manufactured from a solution similar to that used for rayon. The solution is extruded through a slit-die into a coagulating bath of buffered sulfuric acid and cast as a sheet upon a rotating drum, the lower side of which is submerged in the bath. The viscose film formed is transferred to succeeding tanks of warm water to remove the acid. It is desulfurized in a basic solution of sodium sulfide and rewashed. The characteristic yellow color is removed by a hypochlorite bleach, washed thoroughly, and the sheet is then infused with glycerol to impart plasticity to the film. Uncoated cellulose film is not moisture-proof and its packaging uses are limited. It does not seal on automatic machinery, it shrinks on getting wet, and does not prevent moisture loss. It is used for sausage casings, as a base for pressure-sensitive tapes (the adhesives are acrylic copolymers), and as a release agent in molding resins. One great advantage is that it is biodegradable.

Moistureproof cellulose films are prepared by coating one side with nitrocellulose lacquer or a polyvinylidene chloride copolymer solution. The coated films can be printed, and are still biodegradable, although the time required is a little longer.

The manufacture of transparent cellulose acetate sheeting comparable with cellophane is by extrusion of an acetone solution of the required properties through a narrow slit onto a rotating drum, where, in the presence of warm air, the acetone solvent evaporates. The resulting sheet is pliable and moistureproof and is used for photographic film.

POLYOLEFINS. Polyethylene films are made by melting the polymer and extruding it by either slit-die or blow extrusion. The slit-die process produces flat sheets of film by extruding

[23]Briston and Katan, *Plastics Films*, Wiley, New York, 1974; Oswin, *Plastic Films and Packaging*, Wiley, New York, 1975; Nass (ed.), *Encyclopedia of PVC*, Marcel Dekker, New York, 1977.

the molten polymer through a slit-die into a quenching water bath or onto a chilled roller. It is essential that the film be cooled rapidly to form only small crystals and thus maintain its clarity. Very high outputs of film with superior optical properties can be obtained by this method.

The blow extrusion process produces tubular film by using air pressure to force the molten polymer around a mandrel. The plastic emerges from the die through a ring-shaped opening in the form of a tube bubble. The extrusion is usually upward, but it can be down or even horizontal. Figure 35.10 shows the main features of the blow extrusion process. Polypropylene film cannot be formed by this air-cooled method because its rate of cooling is too slow and thus large crystalline aggregates are formed. A water-cooled tubular process[24] has been developed that produces clear polypropylene film at about the same cost as cast film.

POLYVINYL CHLORIDE. PVC film is prepared by feeding a plastic mix of polymer, stabilizers, and plasticizers between two heated rolls where it is squeezed into a film. This process is known as calendering and is widely used in the rubber industry (Chap. 36). Calendering produces sheets of better uniformity of thickness compared with extruded sheets. PVC requires plasticization because without a plasticizer the films are very brittle. The simple phthalates are most commonly used for this purpose and often in amounts up to 50 parts per hundred parts resin (phr). Dioctyl phthalate is the lowest weight member of the series that has low enough volatility to be used. This gives a general purpose film which, however, becomes brittle at very low temperatures. Films for low-temperature use are made using aliphatic esters, such as di-2-ethylhexyladipate, for plasticizers. Different plasticizer content

[24]Prall, Cooling Blown Tubular Film, *Modern Plastics* 46 (4) 154 (1969).

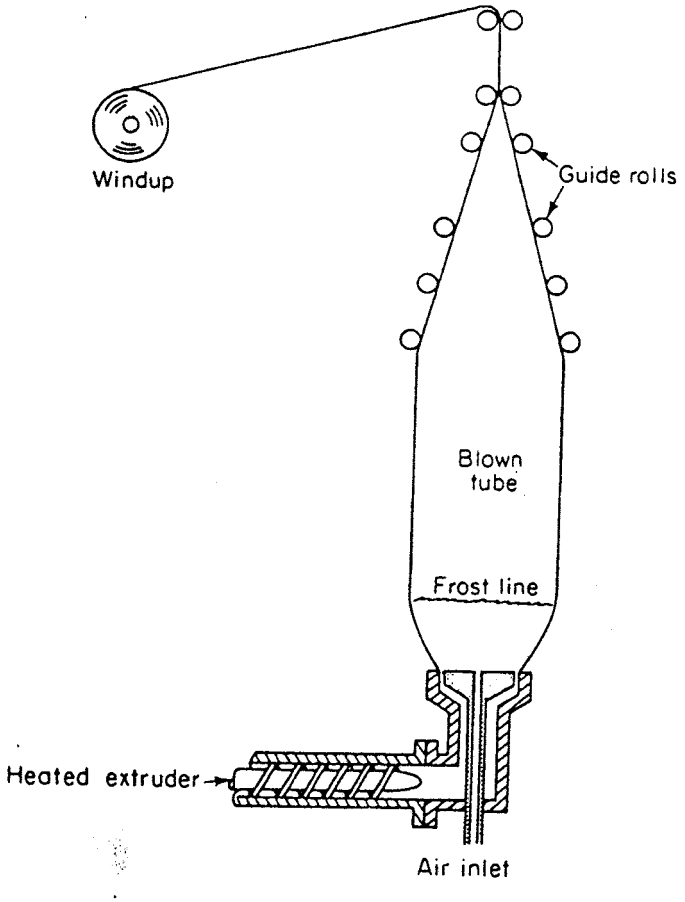


Fig. 35.10. Blown film extrusion process.

produces a range of films suitable for different wrapping applications. Meat wraps require very high concentrations to resist moisture and oxygen. PVC films are not biodegradable and give off HCl when burned thus making environmentally acceptable disposal difficult.

OTHER POLYMERS. Almost any thermoplastic resin can be formed into film by the use of one or the other of the processes described. The choice of process depends largely upon the physical properties of the resin. Polyester and polyamide films are melt extruded. Table 35.1 gives the trade names of some of the common films.

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Chapter 4

Petroleum Processing

Petroleum, the product of natural changes in organic materials over millennia, has accumulated beneath the earth's surface in almost unbelievable quantities and has been discovered by humans and used to meet our varied fuel wants. Because it is a mixture of thousands of organic substances, it has proved adaptable to our changing needs. It has been adapted through changing patterns of processing or *refining*, to the manufacture of a variety of fuels and through chemical changes to the manufacture of a host of pure chemical substances, the petrochemicals.

HISTORICAL. In the United States, Indians used oil seepages in Pennsylvania as medicines, and worldwide, various bitumens were known in Biblical times. Moses' burning bush may well have been an accidentally ignited gas vent. Drake's crude oil well, completed in 1859, showed the world the existence of extensive underground reservoirs of material then mainly useful as a source of kerosene for illuminating lamps. The useless gasoline, which at times had been towed out to sea and burned as a nuisance, gradually became the major product with demand exceeding the supply. Improved quality, as represented by antiknock value, was also desired. The available quantity was extended by converting less desirable fractions into gasoline, first by thermal, later by catalytic cracking processes. Quality improvement in gasoline was brought about by cracking, the tetraethyl lead antiknock properties discovery, polymerization, alkylation, aromatization, and through the gradual awareness that transformations of many kinds were possible by the application of organic processes on a large scale.

Refining has always been pushed along reluctantly by economic factors. For years, many companies viewed refining as a necessary evil to be endured so that they could make money from the more vital production and sale of the crude oil which they produced. Only recently, most companies have come to realize that their purpose is to take a many-component raw material and convert it, at maximum profit, into materials to fulfill the needs of a complex and constantly shifting multiproduct market. In 1930, a company could market only gasoline, kerosene, heating fuel, gas oil, and residuum and show a profit. Today the market is far more complicated, and the marketing decisions are more difficult. Simple fractionation of crude oil into fractions was once sufficient but such simple products would rarely be salable now. Quality needs require upgrading, blending, and consistent quality control of the finished products, although the crudes refined may vary greatly in type and distillate content.

The United States is the largest consumer of petroleum products in the world and has the greatest refining capacity[1] (2,763,800 m^3/day), but is no longer self-sufficient in raw material. The petroleum industry in its design, operation, sales, and executive branches is the largest

[1]Refining capacity is usually stated in U.S. barrels of crude processed. A barrel of oil is 42 U.S. gallons = 0.159 m^3. The capacity figure is from *Hydrocarbon Process.* 61 (9) 13 (1982) and includes 350,000 m^3 of capacity of units in operable shutdown.

employer of chemical engineers. Refining processes have become extremely large and quite complicated. All the branches of this industry are so interrelated and technical that engineering training is required at every level. Needs for technical help are also being enlarged because: (1) sudden price increases for crude and changing markets have required extensive technical readjustment designed to make better use of an expensive and increasingly scarce commodity and (2) the industry has expanded into many other chemical fields—including supplying raw materials formerly supplied by other, smaller sources.

Chemical engineering and petroleum processing have in a very real sense grown up together. Studies on fluid flow, heat transfer, distillation, absorption, and the like were undertaken and applied to a wide variety of materials because of need in the petroleum processing field. Since refined products have physical properties which vary widely from those of water, theory has been refined to include these variables, thus expanding the scope of chemical and mechanical engineering science.

Early refineries used batch stills, small horizontal cylinders, with little or no differential distillation to separate the components, and a condenser. This equipment was originally developed for distilling alcohol. The still produced first gas, then gasoline, then a series of oils of increasing average boiling points and lower value, until a heavy lubricating oil, or asphalt (depending upon the type of crude charged) remained in the still. Modern units operate continuously. First a tubular heater supplies hot oil to an efficient distillation column which separates the material by boiling points into products similar to those obtained with the batch still, but more cleanly separated; then later units convert the less salable parts of the crude (the so-called bottom half of the barrel) into desired salable products. The processes used include various cracking units (which make small molecules from large ones), polymerization, reforming, hydrocracking, hydrotreating, isomerization, severe processing known as coking, and literally dozens of other processes designed to alter boiling point and molecular geometry.

ORIGIN.[2] Most theories concerning the origin of petroleum postulate a vegetable origin with a close relationship to coal. Theory holds that any organic matter may be converted into petroleum under suitable conditions. There is also general agreement that petroleum was formed from organic matter near shore and in marine deposits deficient in oxygen and associated with minerals converted by time and pressure into limestones, dolomites, sandstones, and similar rocks. The concentration of organic matter in the original deposits may not have been high, but petroleum gas and liquids have migrated and gathered in places favoring retention, e.g., sealed-off porous sandstones. Over long periods of time,[3] carbohydrates and proteins are probably destroyed by bacterial action leaving the fatty oils which are more refractory to bacterial or chemical destruction.

EXPLORATION. At one time drilling for petroleum was a hit-or-miss affair and only 1 out of 100 wildcat[4] wells struck oil. Geophysical and seismic work has become highly refined, and when combined with high-speed computers to evaluate the vast amount of data used to locate sites, the chance of drilling success has greatly increased. Geologists and geophysicists studied

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[2]*Science of Petroleum*, vol. 1, 1938, p. 52; Tissot and Welti, *Petroleum Formation and Occurrence*, Springer Verlag, New York, 1978.

[3]Andreev, Bogomolov, Dobryanskii, and Kartsev, *Transformation of Petroleum in Nature*, Pergamon, Oxford, 1968.

[4]A wildcat is a well in an untested area whose location is determined with little scientific assistance.

the occurrence of oil and used scientific instruments to direct their recommendations unti by 1962, 1 out of 9 wells drilled produced either oil, gas, or both. Today's success rate is eve better. Discoveries are now being made in previously explored and rejected areas of difficu geology, such as the Rocky Mountain overthrust area, and the success rate remains high.

Geologists recognized at an early date that petroleum accumulates in pools caught in th anticlinal folds of sedimentary rocks. The gradual accumulation of data from drilling core has guided the test procedures. At scientifically selected sites, wells have been drilled deepe than 6500 m to reach gas or oil.

Seismic analysis can determine the presence of domes and deposits at a considerable dept below the surface. The top of the arch of an anticline or dome is compressed and has a greate density than the surrounding rocks. Figure 37.1 shows the various strata surrounding oil-bear ing rock or sand. Oil and salt also have lower densities than the surrounding rocks. Creatin small seismic waves and measuring their reflected waves at intervals in space and time make possible accurate gravimetric mapping. The finding of a new field is a most serious and exper sive undertaking.

PRODUCTION STATISTICS. The free world's consumption of petroleum in 1982[5] was 2.69 × 10^9 m^3, down from the 1979 peak of 3.04 × 10^9 m^3. Total world consumption was estimate at 5.59 × 10^9 m^3/year. U.S. oil fields produce approximately 14 percent of the world's petro

[5]*World Energy Outlook*, Standard Oil of California, 1982.

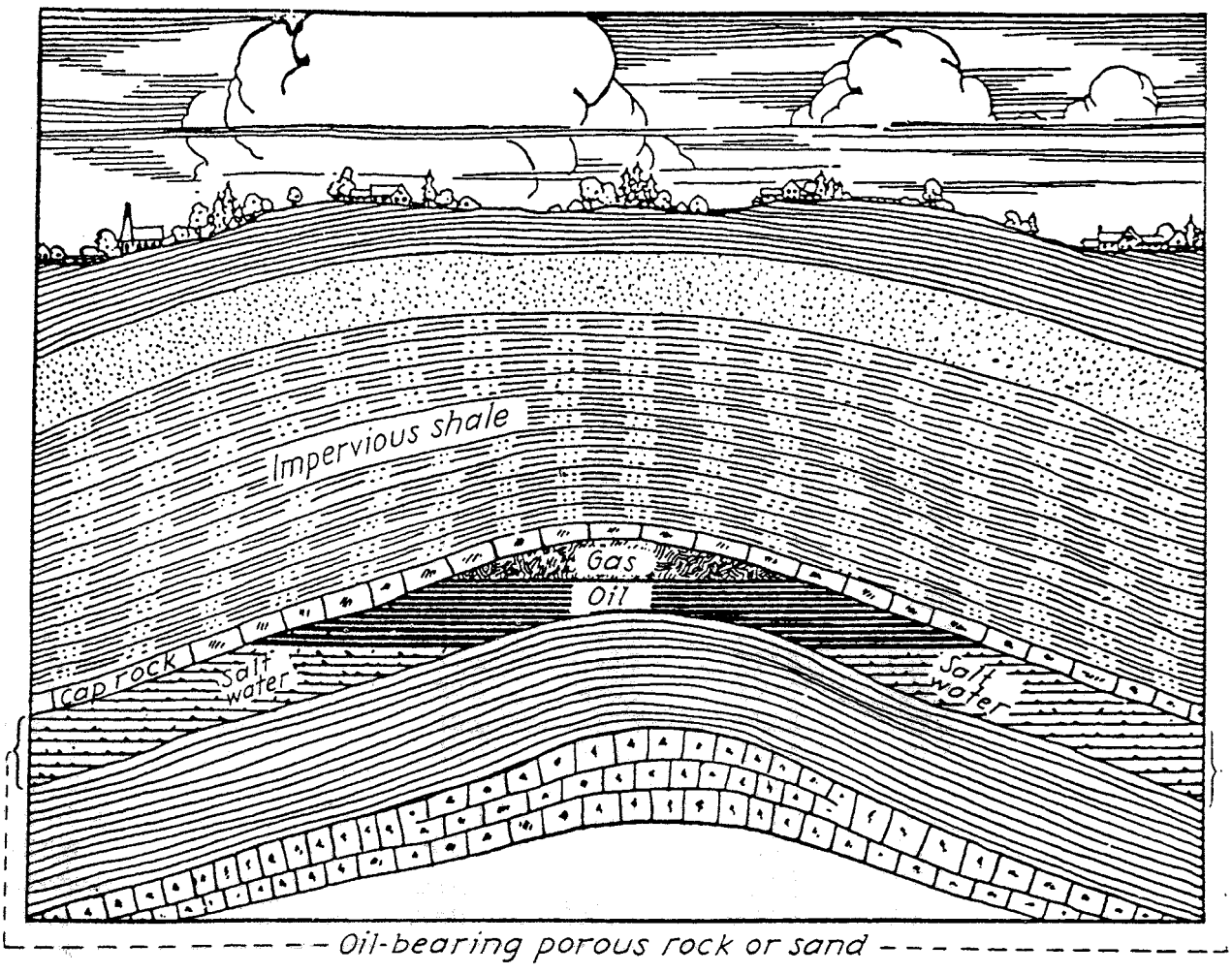

Fig. 37.1. Oil trapped in nature's reservoir. *(American Petroleum Institute.)*

leum as shown in Table 37.1. Most of the free-world fields, except those of OPEC (Organization of Petroleum Exporting Countries), are currently producing at maximum rates. No industry publishes more extensive statistical data than does the petroleum industry through the API (American Petroleum Institute) and other data-collecting agencies.[6] Table 37.2 shows the quantities of refined products currently produced in the United States. Table 37.3 shows the petroleum industry expenditures for new plants and equipment. It is felt that gasoline consumption in the United States has now peaked, so the major new growth will be in the consumption of diesel fuel and kerosene-based jet fuels until these last two will exceed gasoline.

OPEC now provides 50 percent of the total free-world oil production. By 1990,[7] this should be somewhat less as new fields are found in other locations, and as OPEC reaches productive maturity.

RESERVES AND RAW MATERIALS. Estimates of the reserves of such essential minerals as petroleum are inexact, but of vital importance in predicting future trends and in planning.

[6]See various publications by the API and other industry organizations.
[7]*World Energy Outlook,* op. cit.

Table 37.1 World Crude Oil Production by Countries and by Years (in millions of cubic meters; to convert to U.S. barrels multiply by 6.33)

	1977	1978	1979	1980
Algeria	66.5	67.0	66.5	62.9
Argentina	24.8	26.1	27.2	29.1
Australia	24.8	25.0	25.2	22.1
Brazil	9.3	9.3	9.8	10.7
Canada	76.1	75.5	86.1	83.7
China, mainland	108.1	120.1	122.5	122.0
Ecuador	10.6	12.3	12.3	12.3
Egypt	23.9	27.8	28.4	34.0
India	12.0	13.1	14.9	12.6
Indonesia	97.2	94.3	95.0	84.8
Iran	326.6	302.2	177.1	86.9
Iraq	135.4	147.7	197.8	151.8
Kuwait	113.6	122.9	144.3	95.1
Libya	119.0	113.9	119.1	103.3
Malaysia	10.6	12.5	16.3	15.8
Mexico	56.6	69.7	84.2	111.9
Nigeria	120.1	110.1	148.7	119.1
Norway	16.1	20.1	22.1	28.8
Oman	19.6	18.2	17.1	16.6
Peru	5.2	8.7	11.1	10.9
Qatar	25.6	28.0	29.3	27.3
Rumania	17.2	16.3	14.5	13.6
Saudi Arabia	530.6	478.7	549.7	557.7
Trinidad and Tobago	13.3	13.3	12.3	12.3
United Arab Emirates	115.3	105.5	104.8	98.6
United Kingdom	44.1	61.5	88.8	91.8
United States	475.4	502.1	492.0	497.1
U.S.S.R.	633.7	663.8	680.0	700.3
Venezuela	129.1	124.8	135.9	125.3
Total	3360	3391	3533	3338

Table 37.2 U.S. Refinery Production (in millions of m^3; to convert to U.S. barrels, multiply by 6.33)

Product	1965	1975	1978	1979	1980
Still gases*	14,170	17,840	20,388	20,898	20,082
Liquefied refinery gases	17.0	17.3	19.9	19.2	18.9
Gasoline	269	380	418	399	380
Petrochemical feedstocks	9.2	19.4	35.5	40.0	38.0
Kerosene	14.8	8.7	8.9	10.7	7.9
Jet fuel	30.4	50.6	56.3	58.7	58.0
Distillate fuel oil	122	154	184	183	157
Residual fuel oil	42.8	71.7	96.8	97.9	94.8
Asphalt	19.7	22.9	27.5	26.9	22.4
Coke, metric tons	18.9	28.4	29.7	30.1	29.7
Other finished products	38.8	20.8	26.5	25.1	18.6

*In cubic meters of gas (10^3 m^3 = 1.04 t). Calculated from data in *Statistical Abstract of the United States*. 1981.

To make such statistics more reliable, it is customary to use the term "proved reserves" to refer to minerals known to exist in well-defined fields and which are recoverable by present production methods. Not all the petroleum existing underground is recoverable. Heavy crude recovery seldom exceeds 50 percent. Under favorable circumstances, up to 80 percent of lighter crudes may be brought to the surface. Although some is wasted, practically all natural gas can be recovered and utilized. Proved reserves of the world in 1981 were estimated at 1.03×10^{11} m^3 of which the proved reserves in the United States constituted 4.20×10^9 m^3.

The actual useful size of reserves is dependent upon the recovery techniques used. Ashburn, in 1887, estimated that wasteful production techniques in Pennsylvania and New York oil fields would ultimately result in the recovery of only 11 to 12 percent of the oil present. If methods now available had been used then, 2 to 2½ times more oil would have been taken out than was actually recovered by natural flow and pumping. The key to the problem is proper conservation and utilization of reservoir energy. Oil is usually underlaid with water under considerable pressure and overlaid with gas, as shown in Fig. 37.1. Withdrawal of oil from the proper place at a sufficiently low rate allows the pressure to be maintained, saving much pumping energy.

Natural gas or CO_2 can be returned to repressure wells. In one instance, a slower rate of oil production and recycling natural gas at 9.6 MPa enabled a net recovery of 70 percent of the oil originally present. This is twice the amount recoverable without repressuring. Natural high-pressure CO_2 is often piped long distances to use in oil fields. Air is not suitable for repressuring, because it causes deterioration in the quality of the oil produced.

Table 37.3 Petroleum Industry Expenditures for New Plants and Equipment (in dollars $\times 10^9$)

Function	1960	1970	1975	1980	1981
Production	1.6	2.0	4.6	11.3	13.4
Transportation	0.2	0.4	0.8	1.0	1.1
Refining and petrochemicals	0.5	1.3	2.6	4.6	5.8
Marketing	0.5	1.0	0.5	0.9	0.8
Other	0.1	0.5	1.1	2.8	4.1
Total	2.9	5.2	9.6	20.6	25.2

SOURCE: *Statistical Abstract of the United States*, 1981.

Water introduced into a central well can force oil out to surrounding wells. Such *water flooding* is extensively practiced. Some abandoned areas have been made into good producers by this technique.

Steam flooding is in extensive use in some heavy crude oil fields. The addition of heat and or surface-active materials and polymers *(micellar flooding)* also contribute to better recovery. Such treatments are expensive. Underground combustion of some of the oil to heat up the rest so that it will flow more readily is an established method. "Operation Plowshare" tested a nuclear explosion to release natural gas from rock. It was a modest technical success, but an economic failure.

For years, wells drilled into hard limestone have been shot with nitroglycerin because the resulting fissures and fractures increased the drainage of oil into the reservoir. Hydraulic fracturing with gels containing solid propping agents to hold the formed fissures open is much in vogue. The Plowshare explosion was an extension of the idea of opening channels in otherwise relatively impervious materials. Today, almost every well drilled into a limestone formation has the drainage channels enlarged by treatment with inhibited (to prevent iron corrosion) hydrochloric acid. Explosive treatment followed by acid treatment is also common. The oil service industry has grown to meet these problems,[8] which are distinctly different from drilling problems. This technically oriented group has become a major user of hydrochloric acid and a great many other chemicals. Some fields do not produce at all until after treatment. The movement of oil underground is controlled by its viscosity and surface tension. Gas dissolved in the oil reduces both, another reason to maintain reservoir pressure, since increased gas pressure means more gas dissolved and better fluid properties.

Offshore drilling has resulted in many new wells and is becoming increasingly important as as an area promising new fields after the present ones are gone.

TAR SANDS.[9] Canadian tar sands are being worked to produce a heavy crude, but processing difficulties due to the arctic environment and excessive government interference have made the enterprise a technical success but marginal economically. Major tar sands deposits exist in the United States in California, Kentucky, Texas, and Utah. Canadian reserves have been estimated to contain 6.3×10^{10} m^3 of heavy crude; the United States has 5.69×10^9 m^3 with only about 15 percent recoverable with current methods and at current prices. Several small pilot units are testing technology and the market. Most recover the crude by steaming.[10] Ultrasonics are also being applied.

OIL SHALE. The oil in tar sands is merely mixed with the sands, but in shale the oil is chemically combined with the rock material forming an entity known as kerogen. Kerogen reluctantly gives up its heavy oil which contains higher percentages of nitrogen and sulfur than ordinary crude. Many processing methods have been suggested and several piloted. Klass[11] summarizes them.

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[8]Mathews, The Challenge of Oil Field Chemicals, *CHEMTECH* 10 (12) 756 (1980).

[9]McIntyre, Giant Oil Plant Comes on Stream, *Chem. Eng.* 85 (20) 123 (1978); Oil Recovery Is Higher in New Tar-Sands Route, *Chem. Eng.* 87 (25) 37 (1980).

[10]Chilingarian and Yen (eds.): *Bitumens, Asphalts, and Tar Sands*, Elsevier, New York, 1978.

[11]Klass, Synthetic Crude Oil from Shale and Coal, *CHEMTECH* 5 (8) 499 (1975); Parkinson, New Ways to Process Oil Shale, *Chem. Eng.* 89 (4) 37 (1982).

The difficulties in commercializing a shale oil process are formidable.[12] Each ton of rock processed yields less than 0.2 m^3 of oil, leaving a great volume of solid to be disposed of. The solids contain soluble constituents such as trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), nahcolite ($NaHCO_3$), dawsonite [$Al_2(CO_3)_3 \cdot Na_2CO_3 \cdot nH_2O$], and halite (NaCl). While these materials have value, they are in crude form, and at present they are mainly a difficult disposal problem. Table 37.4 shows the reason for the continued interest in this major national resource.

Major shale deposits occur in Colorado, Utah, and Wyoming with scattered smaller deposits in the eastern states of Indiana, Kentucky, Ohio, and Tennessee. Most deposits are on government-owned land in arid regions. To properly evaluate the commercial promise of shale oil, mining and processing methods must be put into motion to produce at least 5000 to 8000 m^3/day of crude to run over a period long enough to permit full return on the investment (20 to 30 years). Such enterprises cost several billion dollars. Several groups have started and later abandoned projects, but about a half-dozen projects appear likely to be put into production soon, marking the start of a real shale-oil industry. The OPEC oil price increase has made consideration of plants now economically possible. In situ processing and several new mining-retorting processes are under study.[13] The following processes currently command attention, each (except Nos. 4 & 5) can be applied to raw or beneficiated rock.

1. Solids-to-solids heating.
2. Gas-to-solids heating with internal gas combustion.
3. Gas-to-solids heating with external heat generators.
4. In situ retorting with combustion heating.
5. In situ retorting with radio-frequency heating.

With all the attention now being given to the problem, it seems certain that a new industry is about to be created here, but when, and how, it will become economically viable is impossible to predict.

TRANSPORTATION. In the United States a great pipeline transportation system moves a tremendous tonnage of petroleum and natural gas. The pipeline has reached its maximum application east of the Rocky Mountains, where trunk lines, branch lines, and pumping stations form an extremely complex system. The pipeline is the most economical method for trans-

[12]Taylor, Oil Shale Commercialization: the Risks and the Potential, *Chem. Eng.* 88 (18) 63 (1981).

[13]Parkinson, New Ways to Process Shale Oil, *Chem. Eng.* 89 (4) 37 (1982).

Table 37.4 Fossil Fuel Resources of the United States (in EMJ, 10^{18} MJ)

	Estimated in Place	Known or Proved Recoverable
Coal	34.8	8.63
Shale oil and bitumens	9.52	0.48
Natural gas and natural gas liquids	2.93	0.33
Crude oil	2.53	0.23
Total	49.8	9.67

SOURCE: Calculated from data in Klass, Synthetic Crude Oil from Shale and Coal, *CHEMTECH* 5 (8) 499 (1975).

porting natural gas. At regular intervals pressure-booster stations are located, using a small part of the gas to drive gas engines connected to compressors.

The United States has at present over 313,000 km of petroleum pipelines and 1,691,000 km of natural-gas lines.

The growth in use of foreign crude oil has spawned a great shipping industry which has constructed mammoth tankers, some as big as 400,000 deadweight metric tons and carrying over 500,000 m^3 of crude. Refined products are also carried by pipelines, barges, railroad tank cars, and motor tank trucks. Storage of products, some of them under high pressure and all of them highly flammable, has been standardized until now the fire hazard is quite small. Some LPG (liquefied petroleum gas) is stored underground.

CONSTITUENTS OF PETROLEUM

Crude petroleum is made up of thousands of different chemical substances including gases, liquids, and solids and ranging from methane to asphalt. Most constituents are hydrocarbons, but there are significant amounts of compounds containing nitrogen (0 to 0.5%), sulfur (0 to 6%), and oxygen (0 to 3.5%).[14]

The API has joined other groups in an extensive and expensive study to identify the actual constituents of petroleum and has identified over 200 compounds.[15] In the following section, an attempt is made to give some idea of the quantities of a given identified compound contained in several different U.S. crudes. The figures given are volume per volume percentages for (in order) Ponca, Okla. (PO), East Texas (ET), and Bradford, Okla. (BO), crudes which have been studied extensively. No one constituent exists in large quantity in any crude.

ALIPHATICS, OR OPEN CHAIN HYDROCARBONS

n-Paraffin Series or Alkanes, C_nH_{2n+2}. This series comprises a larger fraction of most crudes than any other. Most straight-run (i.e., distilled directly from the crude) gasolines are predominantly *n*-paraffins. These materials have poor antiknock properties. Examples are *n*-hexane (±2% all samples) and *n*-heptane (PO = 2.5, ET = 1.7, BO = 2.5% v/v). As gasolines, these materials knock badly.

Iso-paraffin Series or Iso-alkanes, C_nH_{2n+2}. These branched chain materials perform better in internal-combustion engines than *n*-paraffins and hence are considered more desirable. They may be formed by catalytic reforming, alkylation, polymerization, or isomerization. Only small amounts exist in crudes, e.g., 2- and 3-methylpentanes (0.8, 1.5, 0.9%), 2,3-dimethylpentane and 2-methyl hexane (1.2, 1.3, 1.3%).

Olefin, or Alkene Series, C_nH_{2n}. This series is generally absent in crudes, but refining processes such as cracking (making smaller molecules from large ones) produce them. These relatively unstable molecules improve the antiknock quality of gasoline, although not as effectively as iso-paraffins. On storage they polymerize and oxidize, which is undesirable. This very tendency to react, however, makes them useful for forming other compounds, petrochemi-

[14]ECT, 3d ed., vol. 17, 1982, p. 119.

[15]American Petroleum Institute Research Projects APRIP 6 to 60.

cals, by additional chemical reactions. Ethylene, propylene, and butylene (also called ethene, propene, and butene) are examples. Cracked gasolines contain many higher members of the series.

RING COMPOUNDS

Naphthene Series or Cycloalkanes, C_nH_{2n}. This series, not to be confused with naphthalene, has the same chemical formula as the olefins, but lacks their instability and reactivity because the molecular configuration permits them to be saturated and unreactive like the alkanes. These compounds are the second most abundant series of compounds in most crudes. Examples are methylcyclopentane (0.95, 1.3, 0.5%), cyclohexane (0.75, 0.66, 0.64%), dimethylcyclopentanes (1.75, 2.0, 1.0%), and methylcyclohexane (1.8, 2.4, 2.0%). The lower members of this group are good fuels; higher molecular weight ones are predominant in gas oil and lubricating oils separated from all types of crudes.

Aromatic, or Benzenoid Series, C_nH_{2n-6}. Only small amounts of this series occur in most common crudes, but they are very desirable in gasoline since they have high antiknock value, good storage stability, and many uses besides fuels. A few special crudes (Borneo, Sumatra) contain relatively large amounts. Many aromatics are formed by refining processes. Examples are: benzene (0.15, 0.07, 0.06%), toluene (0.5, 0.6, 0.5%), ethylbenzene (0.18, 0.2, 0.9%), and xylene (0.9, 1.1, 1.0%).

LESSER COMPONENTS. Sulfur has always been an undesirable constituent of petroleum. The strong, objectionable odor of its compounds originally brought about efforts to eliminate them from gasoline and kerosene fractions. Chemical reactions were at first directed at destroying the odor. Later it was found that sulfur compounds had other undesirable effects (corrosion, reducing the effect of tetraethyl lead as an antiknock agent, air pollution). At present, wherever possible, the sulfur compounds are being removed and frequently the sulfur thus removed is recovered as elemental sulfur. Nitrogen compounds cause fewer problems than sulfur compounds, are less objectionable, and are generally ignored.

With the general adoption of catalytic cracking and finishing processes, it was discovered that the occurrence of metals present only in traces (Fe, Mo, Na, Ni, V, etc.) was troublesome as they are strong catalyst poisons. Now methods to remove these substances are being perfected. Salt has been a major problem for many years. It is practically always present in raw crude, usually as an emulsion, and must be removed to prevent corrosion. It breaks down on heating in the presence of hydrocarbons to produce hydrochloric acid. Mechanical or electrical desalting is preliminary to most crude-processing steps.

Petroleum crudes vary widely, each kind requiring different refining procedures. The terms paraffin base, asphalt (naphthene), and mixed base are often applied to differentiate crudes on the basis of the residues produced after simple distillation. A "characterization factor"[16] is also used to describe the properties of a crude with mathematical accuracy.

Pure chemical compounds are not regularly separated by refining processes. Some of the simpler, low molecular weight ones are isolated for processing into petrochemicals. Most petroleum products are mixtures separated on the basis of boiling point ranges and identified by the ultimate uses to which they are well adapted. Figure 37.2 shows the overall relationship between refining processes and refined products.

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[16]Nelson, *Petroleum Refinery Engineering*, 4th ed., McGraw-Hill, New York, 1958

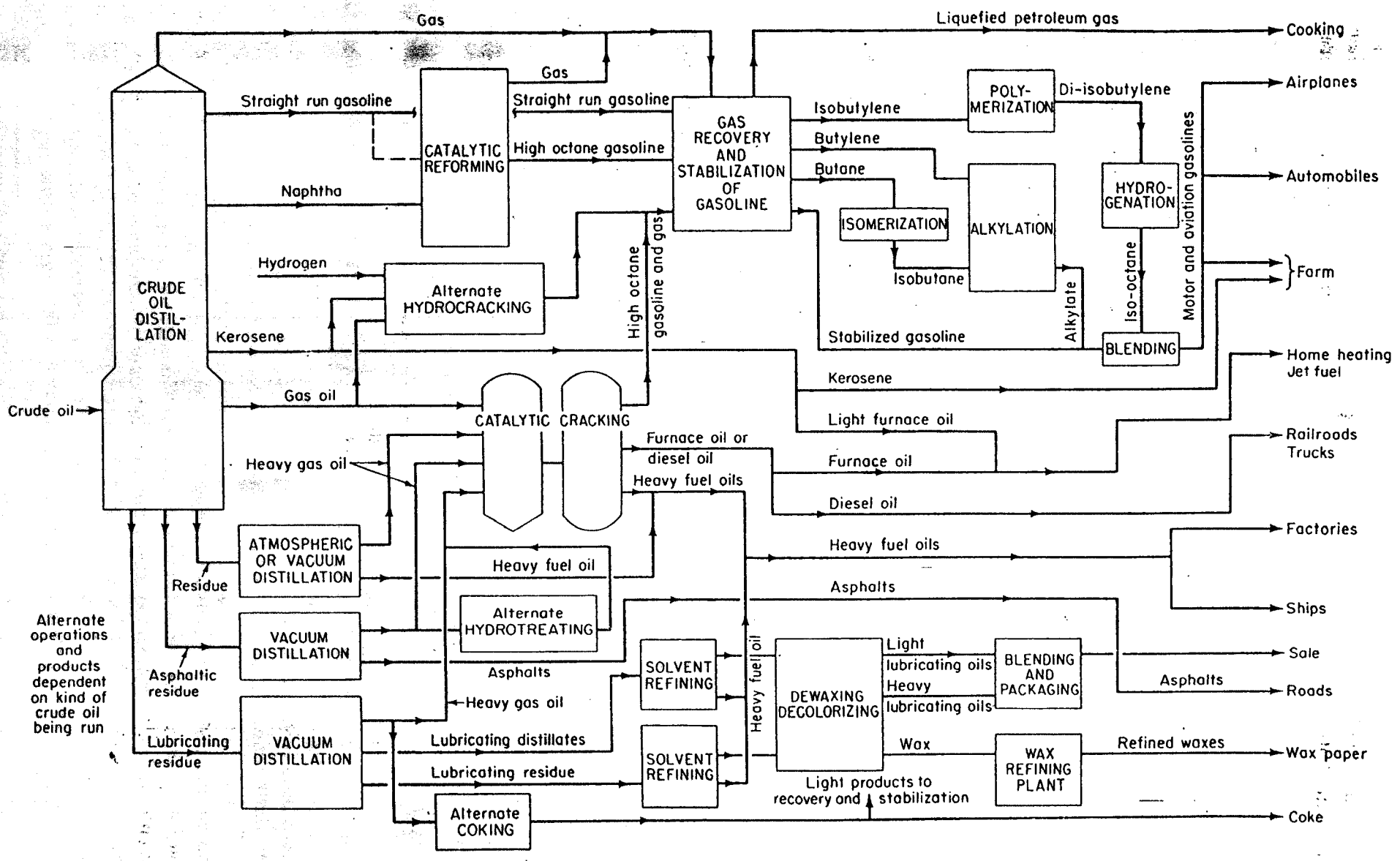


Fig. 37.2. Generalized overall refinery from crude oil to salable products. *(American Petroleum Institute.)*

Common refinery fractions are:

Natural (or casing-head) gasoline and natural gas
LPG
Light distillates
Motor gasolines
Solvent naphthas
Jet fuel
Kerosene
Light heating oils

Intermediate distillates
Heavy fuel oils
Diesel oils
Gas oils
Heavy distillates
Heavy mineral oils (medicinal)
Heavy flotation oils
Lubricating oils

Waxes (candles, sealing, paper treating, insulating)
Residues
Lubricating oils
Fuel oils
Petrolatum
Road oils
Asphalts
Coke

Natural gas (Chap. 6) occurs as accumulations in porous, underground reservoirs with or without accompanying crude. Natural gas was discovered in the United States in the early 1800s, although it had been known elsewhere for centuries. For a time, much natural gas was wasted, but now it is a most important fuel and petrochemical feedstock. "Wet" gas contains vapors of hydrocarbons in the gasoline boiling range, and at one time was simply stripped of its gasoline content, then wasted. The condensed liquid obtained from wet gas is commonly known as natural gasoline. Gas reserves are being discovered at a greater rate than gas consumption. The free world reserves are now (1982) estimated at 48.8×10^{12} m^3. This is a 49-year supply[17] at 1981 production rates. In 1981 1.6×10^{12} m^3 was added to the reserve; consumption was 1.03×10^{12} m^3. Natural gas is composed chiefly of paraffin series hydrocarbons from C_1 through C_5 with CO_2, N_2, and sometimes He as diluents. The most important products obtained from natural gas are fuel, LNG (liquefied natural gas), natural gasoline, carbon black, helium, hydrogen, synthesis gas, and many petrochemicals.

NATURAL GAS LIQUIDS. Gasoline condensed from natural gas contains fewer high-boiling constituents than that obtained from straight-run refining of crude and is, therefore, considerably more volatile. The term natural,[18] or casinghead, gasoline is applied as a special name to distinguish it. While the antiknock properties are only fair, the volatility makes natural gasoline desirable for blending into fuels for use in winter. High volatility makes for easy starting.

Gas withdrawn from underground reservoirs under pressure carries with it lighter components vaporized from the crude oil with which it has been in contact. The composition of the natural gas liquids obtained by condensing these components is determined in large degree by the composition of the crude. Natural gasoline and natural gas liquids are now major petrochemical feedstocks. Isomerization of natural gasoline produces large quantities of isobutane and isopentane which are then reacted with light olefins such as butylene to furnish high antiknock alkylated gasoline.

Because of the demand for high-octane (antiknock) fuel, readily made from natural gas liquids, and of the continuing demand for petrochemical feedstocks, essentially all natural gas is stripped of its condensable material. The individual components are separated by (1) refrigerated absorption, (2) low-temperature distillation, (3) adsorption, or (4) one of the new membrane separation processes. A refrigeration process designed to separate ethane, propane, and natural gas with a high (80+ percent) percentage of the ethane recovered is shown in

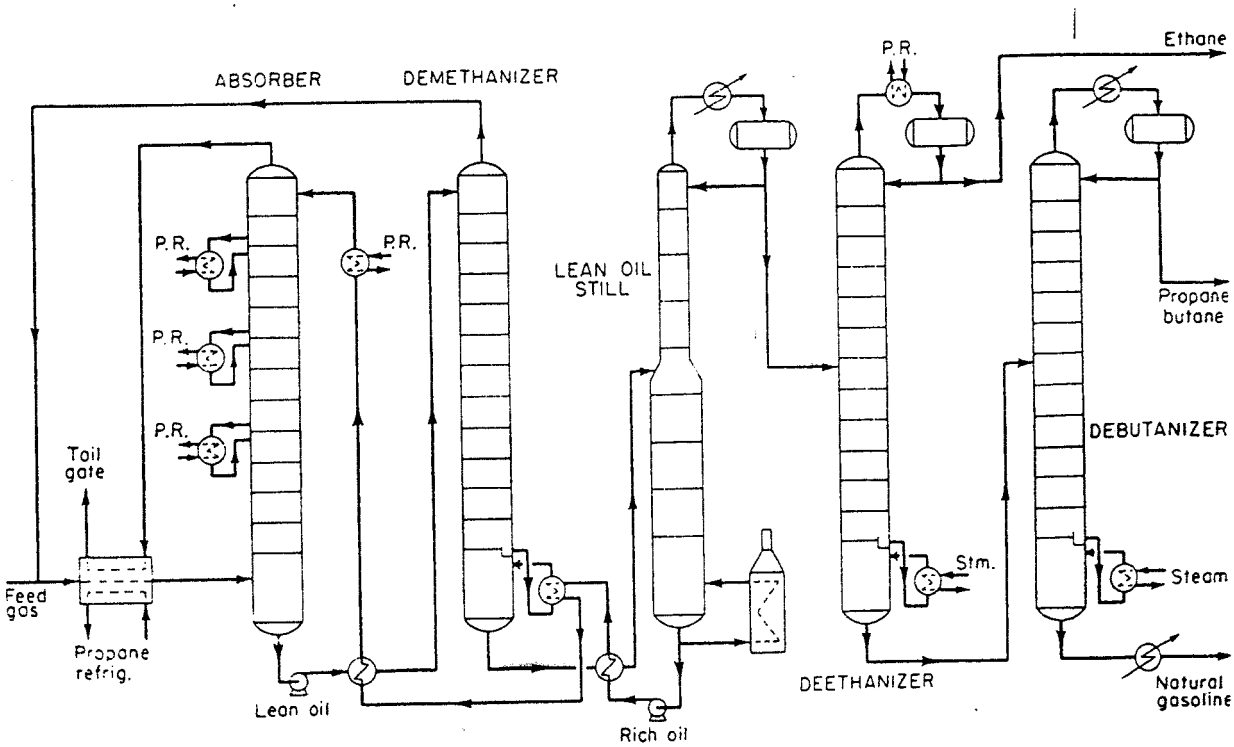
[17] *World Energy Outlook*, op. cit.

[18] Campbell, *Gas Conditioning and Processing*, 4th ed., 2 vols., Petroleum Publ. Co., Tulsa, Okla., 1976.

Fig. 37.3. During the 1970s, many extremely large plants (6×10^7 m^3/day) were built, but smaller plants (4×10^6 m^3/day) are now being considered, and plants using membranes may make even smaller plants practical. Plants such as these operate at −35 to −45°C and use propane as a refrigerant. Absorption processes are less used now than formerly, although some are used in combination with low-temperature fractionation. Low volatility gas oil selectively absorbs the higher molecular weight components which can then be separated in a stripper. Activated carbon or similar adsorbents can also be used and regenerated by heating or pressure swings. Membrane separation processes, not yet thoroughly developed, use diffusion rates through membranes to effect separation.

Refinery Gases. The highest volume of gases generated in the refinery by decomposition of crudes comes from the cracking units. Unlike natural gas, these contain significant proportions of olefins. If temperatures and pressures are kept low, these can be collected and used to make petrochemicals. The separation processes are similar to those for natural gas liquids.

Liquefied Petroleum Gases (LPG). For areas not conveniently adjacent to gas lines, compressed gas in cylinders, the so-called bottle gas, makes excellent and convenient fuel. Propane, with a lower molecular weight than butane, requires a higher cylinder pressure, but both are isolated and sold for domestic fuel and increasingly as a cheap, efficient motor fuel. LPG is competitive with most other fuels as presently used.



Natural gas feed	2.83×10^7 std m^3/day	Cooling water	19 m^3/min
Lean oil (100 mol. wt)	38 m^3/min	Operating labor	60 work-h/day
Fuel gas	8.49×10^5 std m^3/day	Liquid products	1.32×10^7 L/day
Electrical power	25,200 MJ		

Fig. 37.3. Natural gas plant (high-ethane recovery) operated by absorption and propane refrigeration. *(M. W. Kellogg Co.)*

PRODUCTS OF REFINING

Precursors of Petrochemicals

As markets change, there is constant alteration in the materials used for the manufacture of petrochemicals. Almost any synthesis desired can be brought about; the problem is to do it at low cost with the equipment available. Table 37.5 shows the unit operations involved. In earlier times, acetylene was used extensively for making petrochemicals, but it is difficult to make and store, so ethylene has now become the principal raw material for further synthesis.[19] Precursors are reactive materials usually made by breaking down larger molecules, called feedstocks. Ethylene is currently being made from LNG, naphtha, gas oil, diesel fuel, ethane, propane, and butane, with coal a possibility soon to be explored, and some testing of liquefied coal already completed. The principal precursors are:

Acetylene	Propylene	Benzene	Xylenes
Ethylene	Butene	Toluene	Naphthalene

Acetylene production is covered in Chap. 7.

The manufacture of *ethylene* from distillates, natural gas, or gas liquids is shown in the generalized flowchart of Fig. 37.4. This is the largest volume organic material. The conditions for its manufacture lie somewhere between those usually thought of as refining and those encountered in chemical production. Extremely large plants are built and being built. Some plants have a production capacity as large as 7×10^8 kg/year. In 1980, 57 percent of ethylene

[19]Kniel, Winter, and Stork, *Ethylene—Keystone to the Petrochemical Industry*, Marcel Dekker, New York, 1980; Brumm, How Will They Feed the Ethylene Plants of the 1990's? *Chem. Bus.*, October 20, 1980, p. 19.

Table 37.5 Unit Operations for Separation of Olefins and Aromatics as Precursors of Petrochemicals

Operation	Based on Differences In:	Product
Vapor-Liquid		
Distillation	Vapor pressure	Ethylene from ethane
Extractive distillation	Polarizability	*n*-Butenes from butanes
Azeotropic distillation	Polarizability	Toluene from aromatics
Absorption	Solubility	Ethane from methane
Liquid-Liquid		
Solvent extraction	Solubility	Benzene from aliphatics
Liquid-Solid		
Crystallization	Melting point	*p*-from other xylene
Extractive crystallization	Clathrate* formation	*n*-Paraffins from other hydrocarbons
Encapsulation	Clathrate formation	*m*-Xylene
Adsorption on molecular sieves	Surface or pore adsorption	*n*-Paraffins from isoparaffins
Vapor-Solid		
Adsorption on molecular sieves	Surface or pore adsorption	Ethylene from ethane

*Clathrates separate primarily on molecular size and shape.

NOTE: In addition to the physical property differentials tabulated here, chemical differentials are employed, e.g., reversible chemical reaction rates or chemical equilibriums, as exemplified by separating pure butadiene from butene, using reaction with cuprous salts.

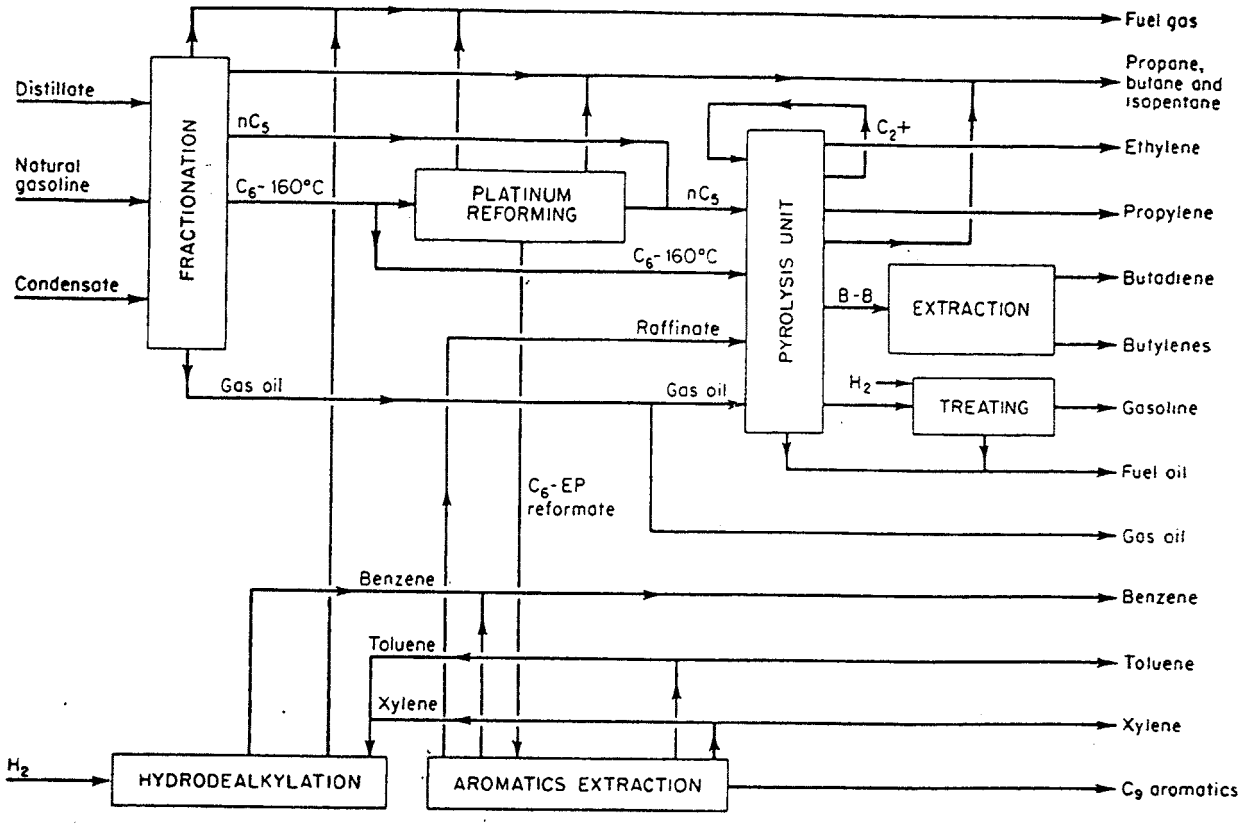


Fig. 37.4. Generalized flowchart for the production of petrochemicals. *(M. W. Kellogg Co.)*

production was based on NGLs; by 1990 the feed is expected to be 60% light hydrocarbons and 40% refinery products.[20] The material to be processed (cracked) is diluted with an inert gas (usually steam) at around 925°C with a residence time of 30 to 100 ms which yields a mixed product which must be separated to be useful. The gases are rapidly quenched, chilled, dehydrated, and fractionated to yield high-purity individual components and unwanted material for recycling. Changing feedstocks and conditions alter the product composition, e.g., butylene or propylene could be made the primary product, if desired. The flowchart of Fig. 37.5 shows the manufacture from refinery gas with the analysis (in percent): methane,

[20]Kniel, op. cit.

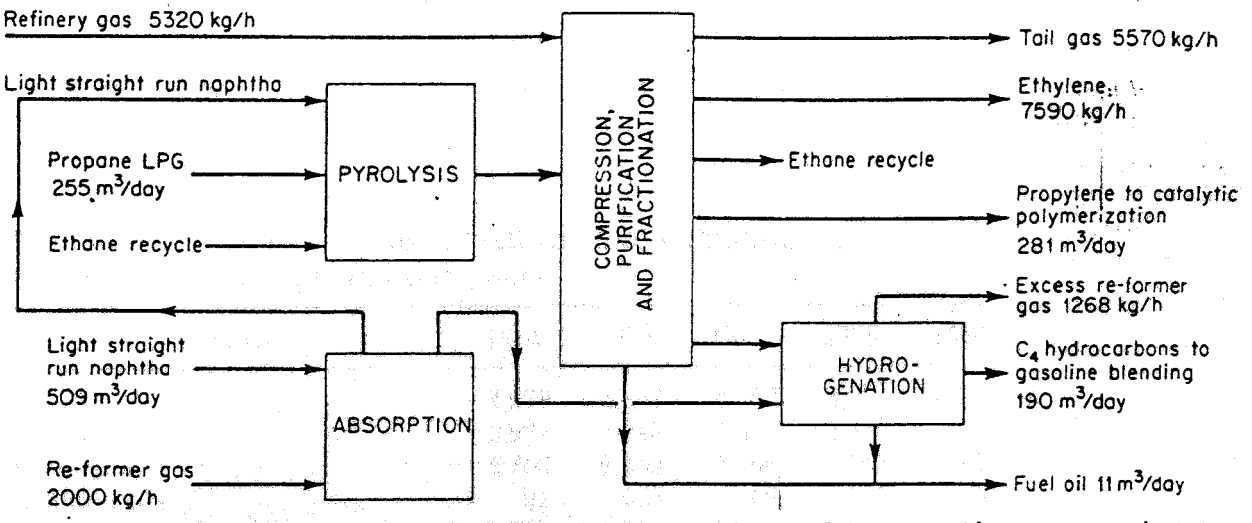


Fig. 37.5. Flowchart for ethylene and propylene production from refinery gas. *(Chem. Eng. and M. W. Kellogg Co.)*

25; hydrogen, 19; ethane, 15; ethylene, 7; propane, 12; and propylene, 6, with the remainder N_2, CO, CO_2, H_2S, and higher hydrocarbons. LPG, high-run gasoline, and ethylene recycle may be added to this. Ethylene production in 1982 was 13.6×10^9 kg/year, but plant capacity was 18.6×10^9 kg/year. Much of the idle capacity was designed for naphtha or gas oil feed, which have become more expensive than light hydrocarbons as a source of ethylene.

A high-severity short-time crack of naphtha feedstock yielded[21] a mix containing (in percent): hydrogen, 1.2; methane, 15.2; acetylene, 1.3; ethylene, 31.8; ethane, 1.2; propadiene, 1.2; propylene, 11.6; propane, 0.3; butadiene, 4.7; butylene, 2.2; and C_{5+} liquids, 27.7.

The increasing cost of light feedstocks and the demand for naphthas for other uses have caused increasing attention[22] to be paid to heavier fractions such as vacuum gas oils, which have become a glut on the market. Both in the United States and abroad, extensive experiments have shown that the production of olefins from such heavy feedstocks, even heavy crude, is possible and will take place when economic conditions warrant it.

Propylene[23] is rarely produced except as a coproduct with ethylene. Steam cracking of ethylene produces most of it, and virtually all of it is used for polymer production. The remainder, used mostly for chemical production, comes from oil refinery fluid catalytic crackers. Refinery propylene is used mainly for alkylation. Production in 1982 was 7.3×10^9 kg/year with a plant capacity of 10.4×10^9 kg/year.

Aromatics are usually thought of as coal-derived, but the amount from that source in 1980 was almost vanishingly small, 4 percent of the benzene, 0.9 percent of the toluene, and only 0.1 percent of the xylenes. Table 37.6 gives statistics for U.S. production, and Fig. 37.6 shows the interrelation between uses and sources. Benzene can be made by *dehydrogenation* of cyclohexane or substituted cyclohexanes, by *aromatization* of methylcyclopentane, and by *demethylation* of toluene or xylenes. The demand for aromatics is large and attention is being given to find catalysts to produce more BTX (benzene-toluene-xylene) for chemical and high-grade fuel use. Toluene is recoverable, as such, from a few stocks, but most is made by dehydrogenation of naphtha; e.g., methylcyclohexane is dehydrogenated to toluene. This can then be demethylated to benzene, if desired.

Naphthalene is used in smaller quantities than the lighter aromatics, but with 2×10^7 kg used in 1981, its consumption is far from trivial. Six U.S. plants have a combined capacity of

[21]Prescott, Pyrolysis Furnace Boosts the Ethylene Yield by 10–20%, *Chem. Eng.* 82 (14) 52 (1975).

[22]Baldwin and Kamm, ACR Process for Ethylene, *Chem. Eng. Prog.* 79 (1) 68 (1983); Fujita et al., Olefins from Heavy Oils, *Chem. Eng. Prog.* 79 (1) 76 (1983).

[23]Spitz, Propylene—Key Question of the Future, *Chem. Eng. Prog.* 71 (11) 13 (1976).

Table 37.6 U.S. Petroleum-Based Aromatic Production (in millions of kilograms per year)

Product	1974	1976	1977	1978	1980
Benzene	4,679	4,467	4,562	4,774	6,510
Toluene	2,977	3,245	3,317	3,428	3,308
Xylenes	2,760	2,489	2,796	2,915	3,134
Naphthalene	91	255	69	71	46
Other aromatics and naphthenes	1,551	1,991	1,434	1,874	1,815
Grand total	12,058	12,447	12,178	13,062	14,813

From data of the U.S. International Trade Commission, annually.

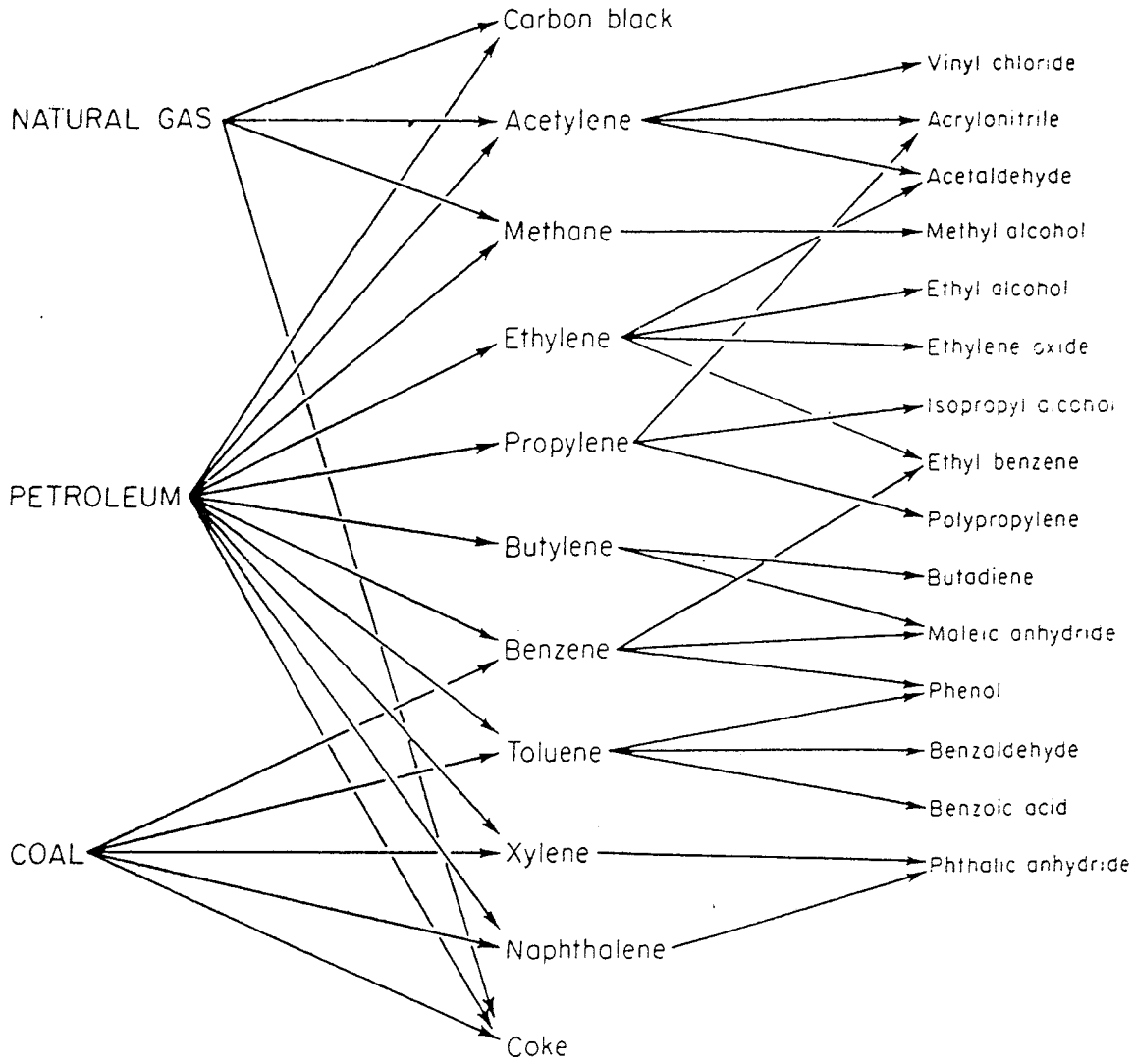


Fig. 37.6. Interrelationship of precursors from natural gas, petroleum cuts, and coal. *(Marshall Sittig.)*

3.13×10^7 kg/year. Dealkylation of a selected reformate stream using chromate-aluminum carbide catalyst with a 10-s exposure gives a product which is purified to be purer than that formed from coal tar. The Hydeal process by Ashland Oil Co. is one of the processes used.

LIGHT DISTILLATES. Aviation gasoline, (automobile) motor gasoline, naphthas, petroleum solvents, jet-fuel, and kerosene are the fractions generally regarded as light distillates. Any given refinery rarely makes all of them. Gasoline is the most important product, and around 45 percent of the crude processed now ends up as gasoline. When the compression ratio of a motor is relatively high, the fuel can detonate in the cylinder causing noise (knock), power loss, and ultimately engine damage. Branched chain and aromatic hydrocarbons greatly reduce the tendency of a fuel to cause knocking. *n*-Heptane knocks very readily; 2,2,4-trimethyl pentane (formerly known as iso-octane) is an extremely antiknock fuel. The *octane number*, a measure of the suitability of a fuel for high-compression engines, is the percentage of iso-octane which, when added to *n*-heptane, knocks in a special test engine to the same degree as the fuel being tested. Certain substances, such as tetraethyl lead (TEL) and tetramethyl lead (TML) can be added to gasoline in very small quantities to raise the octane number dramatically. Because of doubts concerning the safety of lead in the environment, these most useful additives are now restricted or limited. Cleaner burning is achieved by adding intake system detergents.

Aviation gasoline is generally sold in two grades, 100 octane and 80 octane with the major demand for 100 octane. Some compounds or mixtures are now known which either have octane numbers above 100, or blend as if they had numbers over 100, so avgas is a blend of catalytically cracked gasoline, high-quality alkylate, and TEL.

The amount of sulfur that can safely be permitted in gasoline is debatable, but sulfur is always undesirable. Concentrations as high as 0.2% do not cause serious corrosion, but regulations usually limit sulfur to around 0.1%. TEL effectiveness is sharply reduced by the presence of sulfur or sulfur compounds.

When the Environmental Protection Agency (EPA) reduced the lead (as TEL) allowable in some gasoline and required its absence from most, refineries faced a difficult problem. The amount of branched chain and aromatic constituents in regular gasoline had to be increased to keep the antiknock high after the lead was removed. The problem was resolved by utilizing more severe cracking, by adding octane boosters such as methyl tertiary butyl ether (MTBE), methanol, and ethanol. This continues to be a problem for gasoline suppliers.

Originally, water whiteness in gasoline was an indication of good quality distillation, but this hasn't been true for nearly 50 years. Consumers still prefer clear colorless products, but it is expensive and pointless to produce them. Oil-soluble dyes are now added to give uniformity of color and to identify the company from which the fuel came.

The term *naphtha* is loosely applied to materials with boiling ranges between gasoline and kerosene. There are a number of specialty naphthas, e.g. varnish maker's and painter's naphtha (VM&P), dry cleaning solvent, rubber solvent, etc. Some naphthas are used for ethylene feedstocks, but the cost is high and the use diminishing. The military uses a naphtha-based jet-fuel known as JP-4 extensively.

Kerosene was originally used for lamps and home heating, but most is now used as jet fuel for airplanes.

INTERMEDIATE DISTILLATES. These include gas oil, light and heavy domestic furnace oils, diesel fuels, and distillates used for cracking to produce more gasoline. These distillates are used mainly for transportation fuels in heavy trucks, railroads, small commercial boats, standby and peak-shaving power plants, farm equipment, and wherever diesels are used to produce power. Home heating furnaces use these distillates. Asphalt is "cut back," i.e., made less viscous, with them. The name gas oil originated with their use to produce illuminants to improve the lighting value of manufactured town gas; this use has disappeared. The heavier grades are especially suited for cracking to produce motor gasoline. Yields of gasoline as high as 1.08 L per liter of distillate fed are obtained. The major volume goes into diesel fuel.

ADDITIVES TO PETROLEUM PRODUCTS.[24] Doubts concerning their environmental effects have reduced the use of additives which have often produced large improvements in performance with tiny additions. In 1972, the use of TEL/TML was over 440×10^6 kg, but by 1982 it had fallen to 143×10^6 kg; it is projected to fall to 91×10^6 kg by 1986. Unleaded gasolines require more alkylates and reformates to maintain their quality. Organophosphates reduce combustion chamber deposits, but their use is also restricted. Corrosion inhibitors are used, and in some cases antioxidants to stabilize the olefins and diolefins, thus reducing the production of engine gum and varnish. Detergents are added to gasoline and lubricating oils

[24]Miles, *Chemical Additives for Fuels*, Noyes, Park Ridge, N.J., 1982; Ranney, *Corrosion Inhibitors*, Noyes, Park Ridge, N.J., 1976; Fuel and Lubricant Additives, I and II, *Lubrication* 63 (1 and 2), Texaco Co., 1977; Satriana (ed.), *Synthetic Oils and Lubricant Additives since 1979*, Noyes, Park Ridge, N.J., 1982.

to promote cleanliness. Some gasolines have over a dozen components. Diesels do not knock in the same manner as gasoline engines, but a *cetane* number is used to measure fuel quality and alkyl nitrates improve it.

HEAVY DISTILLATES. These are converted into lubricating oils,[25] heavy oils for a variety of fuel uses, waxes, and cracking stock. Lubricating oils of high quality can readily be made from paraffin-base oils, but most oils are mixed or naphthene base, and solvent refining is required to produce quality lubes. The Society of Automotive Engineers (SAE) has classified lube oils by means of a number system based on viscosity, change of viscosity with temperature, and severity of service. These numbers are generally used in the United States in selecting and classifying oils. A solvent extraction process for improving lube oil quality is shown in Fig. 37.7, and propane deasphalting is shown in Fig. 37.8. Additives are used extensively to improve the quality of lubes. Among those used are antioxidants, detergents, antifoams, viscosity-index improvers, extreme-pressure agents, and antiscuff agents. Viscosity, pour point, emulsibility, flash point, and resistance to sludging are important properties of lubes, generally determined by technological tests outlined and standardized by the American Society for Testing and Materials (ASTM). Synthetic lubricants,[26] not directly petroleum derived, are now appearing on the market and much re-refined[27] oil is being used.

Refined wax[28] is used industrially, primarily for treating paper, especially for milk cartons. Although there are many uses, synthetic waxes have sharply limited the field. Waxes are usually separated from narrow boiling point fractions, then isolated and purified by crystallization and sweating. Acid treatment or percolation through clay is used to improve the color.

Heavy distillates are used for bunker fuel for ships and in large stationary power plants, but all uses of heavy distillates are declining and the tendency is to use them as cracking stock, crack them severely in coking units (cracking units producing coke as a by-product), and convert them into products for which there is a higher demand and a better price. Sulfur content is a major determinant of the value of heavy distillates, it must be low if the product is to be readily salable.

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[25]Gillespie, Manley, and DiPerna, Making Lube Oils, *CHEMTECH* 8 (12) 750 (1978).

[26]Synthetic Lubricants Poised for Big Growth, *Chem. Eng. News* 58 (21) 12 (1980).

[27]Bright Prospects for Used-Oil Refiners, *Chem. Eng.* 86 (16) 28 (1979); Reynolds et al., From Oil:Oil, *CHEMTECH* 9 (10) 628 (1979).

[28]Wax, *Chem. Week* 101 (15) 61 (1967); Bennett, *Industrial Waxes*, 2d ed., 2 vols., Chem. Publ. Co., New York, 1976.

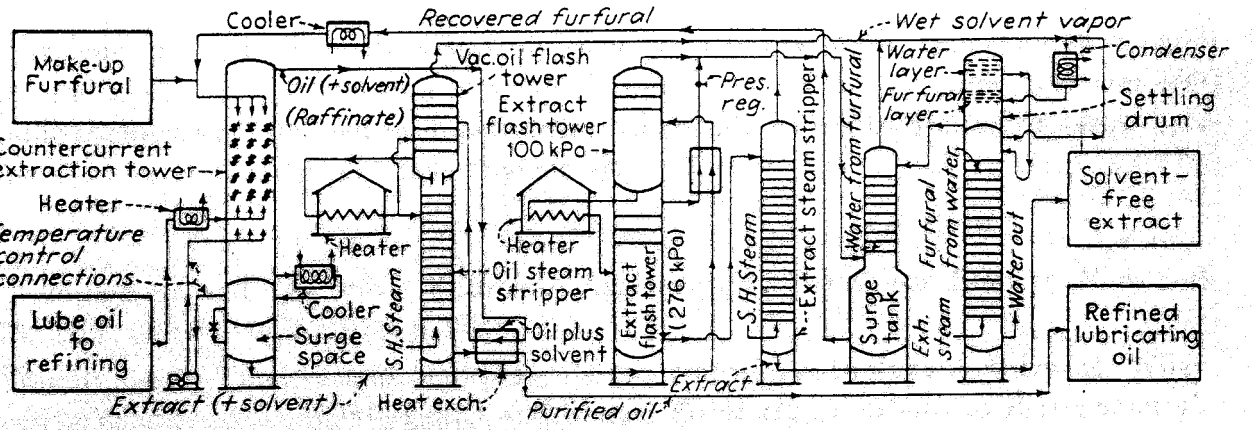

Fig. 37.7. Flowchart for lube oil refinery by furfural extraction.

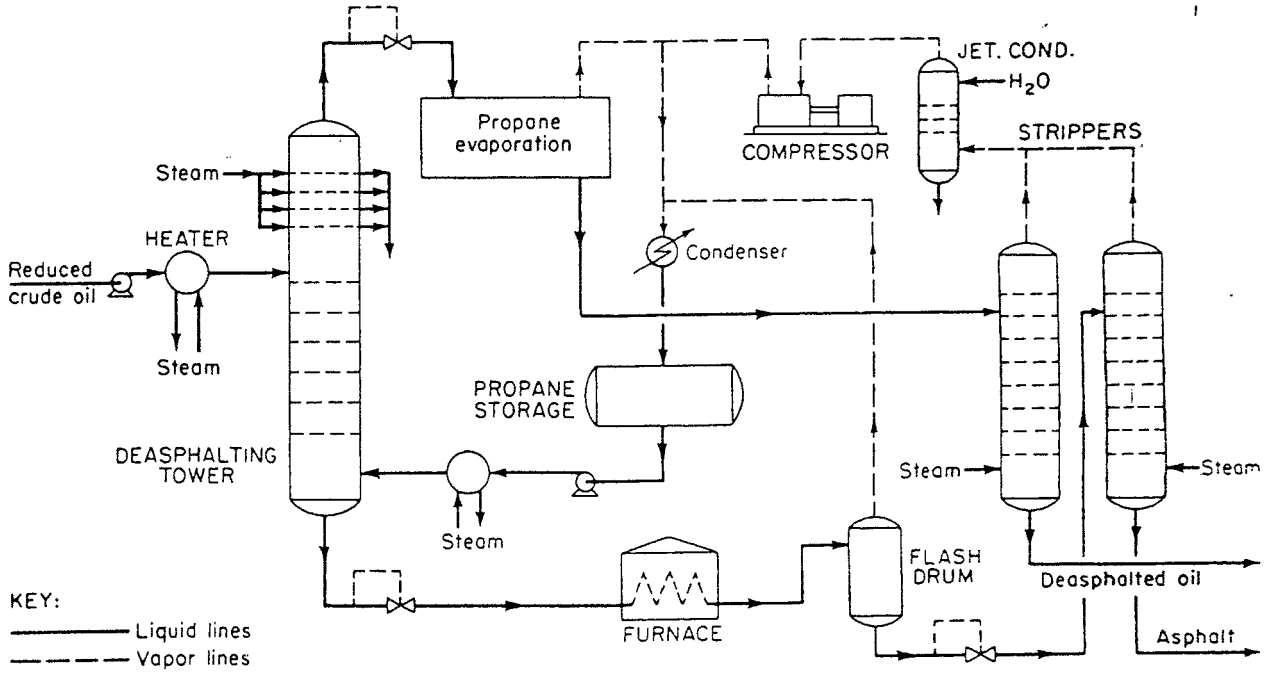

Fig. 37.8. Flowchart for lube oil deasphalting—Kellogg tower process. *(M. W. Kellogg Co.)*

RESIDUES. Some constituents are simply not volatile enough to be distilled, even under vacuum. These include asphalt, residual fuel oil, coke, and petrolatum. These difficultly salable materials are by-products of the refining process, and while many are extremely useful, most are difficult to dispose of and are relatively unprofitable. Petroleum coke is used commercially in making electrodes, in the manufacture of calcium carbide and ceramics, and in paints. Asphalt[29] finds a ready market as a road-paving material, for waterproofing structures, and in roofing material. In early times, most asphalt came from deposits in Trinidad, which are still being worked. Most is now obtained from crude residues. The properties of asphalt are markedly changed by heating it and partly oxidizing it by blowing air through it. The resulting material is known as oxidized, or blown, asphalt and is more viscous and less resilient than ordinary asphalt. It is used for impregnating roofing felt and for grouting. Hard asphalt is also used as a briquetting binder.

Greases, consisting of a divergent group of materials, fall into three classes:

1. Mixtures of mineral oil and solid lubricants
2. Metallic soap-thickened mineral oils
3. Blends of waxes, fats, resin oils, and pitches

Petroleum-derived chemicals, commonly known as petrochemicals,[30] are made from petroleum and natural gas. Production of some of these products is very large, and over 1000 organic chemicals are derived from petroleum (Chap. 38). Examples are carbon black, butadiene, styrene, ethylene glycol, polyethylene, etc.

[29]Chilingarian and Yen (eds.), *Bitumens, Asphalts, and Tar Sands*, Elsevier, New York 1978; ECT, 3d ed., vol. 3, 1978, p. 284.

[30]Rudd, Saeed, Trevino, and Stadtherr, *Petrochemical Technology Assessment*, Wiley-Interscience, New York, 1981; Hatch and Matar, *From Hydrocarbons to Petrochemicals*, Gulf, Houston, Tex., 1981; Maisel, Trends in the Petrochemical Industry, *Chem. Eng. Prog.* 76 (1) 17 (1980).

PROCESSING OR REFINING

Refining is a low-cost operation compared with most chemical processing. Crude cost was formerly far lower than now, but the Organization of Petroleum Exporting Countries (OPEC) raised the price approximately tenfold. Refining profits have been quite moderate percentages of capital costs, comparable with other phases of the chemical industry. Consider the distribution of costs of a liter of gasoline in California in 1982:

Cost of crude (Arabian)	21.4 cents
For Gasoline	
Wholesale price	25.1 cents
State and federal excise tax	2.9
Transportation and storage	1.6
State sales tax	2.1
Dealer margin	3.2
Price at retail pump	34.3
(34.3 cents/L = $1.30 per U.S. gallon)	

Refining involves two major branches, separation processes and conversion processes. Particularly in the field of conversion, there are literally hundreds of processes in use, many of them patented. Even in a given refinery running a single crude, daily changes to accommodate changing markets and changing parameters of the conversion apparatus take place. It is the intention, therefore, of the remainder of this chapter to set forth the more important processes, show their general principles, and indicate the applications to which they may be put. No refinery on any day will operate exactly as shown, but all refineries will operate along the basic lines indicated.

Early refineries separated petroleum components into salable fractions by some type of distillation. Some chemical or heat treatment often followed to improve the quality of the crude product obtained. About 1912, the demand for gasoline began to exceed the supply, and it was presently found that the application of heat and pressure to heavier, unwanted fractions converted the large molecules into smaller ones in the boiling range of gasoline. This process, utilizing a pressure still, became known as cracking. It produced a superior gasoline because more olefins and branched chain hydrocarbons were present in the product than in straight run gasoline. This process, improved by the inclusion of active catalysts and in its methods of processing, continues to be the most important chemical process in use today. Other chemical conversions are also practiced on a very large, but lesser scale. Among them are alkylation, isomerization, hydrogenation, polymerization, reforming, and dehydrogenation.

Refineries were originally batch units with cylindrical underfired shell stills operated as "topping" units.[31] Pumping oil continually through heaters known as pipe or tube stills and separating the constituents in continuous fractionating columns that separate many fractions between gas and asphalt is now universally practiced. Primary separation is followed by various conversion process designed to optimize yields of the more profitable and salable products. Generally this means maximum yield of gasoline. Technologically, it would be quite possible to convert the crude entirely to gasoline, but the cost would be quite prohibitive.

[31]Topping is removal of the more highly volatile constituents, leaving "reduced crude" as a residue.

ENERGY CHANGES. For many years, energy expense for refining has been the most important manipulatable cost. Conservation of heat has been the object of concentrated study. Since the sharp increase in the cost of energy, this study has been intensified. The great needs of the growing petroleum industry led to the careful study of fluid flow, heat transfer, and the properties of petroleum fractions. The industry has generated much scientific data and most of it has been made available to the scientific community. Extensive use of instruments and control systems was first made by the refining industry which now makes extensive use of direct digital control (DDC), a computer system designed to optimize variables.

SEPARATION PROCESSES. The unit operations used in petroleum refining are the simple, usual ones, but the interconnections and interactions may be complex. Most major units are commonly referred to as *stills*. A crude still consists of heat exchangers, a furnace, a fractionating tower, steam strippers, condensers, coolers, and auxiliaries. There are usually working tanks for temporary storage at the unit; frequently there are treating tanks, used for improving the color and removing objectionable components, particularly sulfur; blending and mixing tanks; receiving and storage tanks for crude feed; a vapor recovery system; spill and fire control systems; and other auxiliaries. For the refinery as a whole, a boiler house and usually an electrical generating system are added. A control room with instruments to measure, record, and control, thus keeping track of material which permits heat and material balances, forms the heart of the system. One of the major functions of the instruments is to permit accurate accounting of the materials and utilities used. Many control systems are now connected to computers which do many calculations routinely.

The following unit operations are used extensively in the separative section:

1. ***Fluid flow.*** Fluid flow is an operation that must not permit any unexpected failure because fire and explosion might ensue.

2. ***Heat transfer.*** Transfer coefficients change daily as fouling occurs. Cooling towers become less effective with time. Modern plants check the condition of the exchangers daily against computer records.

3. ***Distillation.*** Originally haphazard, study by the industry and universities revealed the process variables which can now be modeled and optimized with computers. When side streams are withdrawn, they contain undesirable light volatiles which are usually removed in small auxiliary towers by steam "stripping." Tower contacting material, at one time all packing or bubble caps, now consists of a variety of tower "packings" and special trays designed to reduce pressure drop while increasing vapor-liquid contact.

When the difference in volatility between components is too small for separation in a reasonably sized tower, modifications of simple distillation are used. When a solvent of low volatility is added to depress the volatility of one of the components, the separation is known as *extractive distillation*. Butenes are separated from butanes using this principle with furfural as the extractant. When a high-volatility entrainer is used, the process is called azeotropic distillation. Distillation to produce anhydrous alcohol from 95% solution uses benzene to free the azeotrope (Chap. 31), and high-purity toluene is separated using methyl ethyl ketone as the entrainer.

4. ***Absorption.*** is generally used to separate high-boilers from gases. Gas oil is used to absorb natural gasoline from wet gases. Gases which are expelled from gas storage tanks as a result of solar heating are also sent to an absorption plant for recovery. Steam stripping is generally used to recover the absorbed light hydrocarbons and restore the absorption capacity of the gas oil.

5. *Adsorption.*[32] is used for recovering heavy materials from gases. Adsorbents such as activated charcoal and molecular sieves are used. Molecular sieves can select the materials recovered by molecular shape as well as molecular weight; this can be very useful. Energy can be saved by using a pressure swing absorption process wherein the material is released from the adsorbent by changing the system pressure.

6. *Filtration.* Filtration is used to remove wax precipitated from wax-containing distillates. If the cold cake is allowed to warm slowly, the low-melting oils drain (sweat out) from the cake and further purify it. Filtration in the presence of clays is known as contact filtration and has been used extensively for the decolorization of fractions. Types of filters are discussed in Perry.

7. *Crystallization. Before* filtration, waxes must be crystallized to suitably sized crystals by cooling and stirring. Waxes undesirable in lubes are removed and become the microcrystalline waxes of commerce. *p*-Xylene can be crystallized and separated from other C_8 materials by differential crystallization. For most purposes, this operation is both slow and expensive.

8. *Extraction.*[33] Extraction is removal of a component by selectively dissolving it in a liquid. This procedure is very important in preparing high-quality lube oil. Low-viscosity index materials (those whose viscosity changes rapidly with temperature), waxes, color bodies, and sulfur compounds are removed in this way (Fig. 37.7). Adequate mixing must be followed by clean and rapid separation of the two liquid layers. If a proper solvent is available, the mixture separates into two layers, one called the *extract*, which is usually solvent-rich and contains the impurities; the other called the *raffinate*, which should contain the desirable constituents and little solvent.

A process[34] has recently been introduced for extracting asphalt from residuum with, e.g., pentane, enabling such residuums to be used as catalytic cracking stock.

The procedure used when lubricating oil is treated with furfural is shown in Fig. 37.7, the following sequence is involved:

Continuous countercurrent extraction with furfural at 50 to 140°C, depending on the stock used.

Continuous separation of the raffinate from the extract.

Recovery of the furfural by evaporation from the raffinate.

Steam stripping to remove final traces of furfural from the raffinate.

Recovery of the furfural by atmospheric and pressure distillation of the extract.

Steam stripping to clear the extract of solvent.

Fractionation of wet, recovered furfural to give dry solvent for reuse.

Loss of solvent furfural can be cut below 0.03 percent of the solvent recirculated if the system is well run. Other solvents used for processing oil include propane, MEK, liquid sulfur dioxide, cresylic acid, dichlorethyl ether, phenol, and nitrobenzene.

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[32]Breck, Advances in Adsorption, *Chem. Eng. Prog.* 73 (10) 44 (1977); Broughton, Bulk Separations via Adsorption, *Chem. Eng. Prog.* 73 (10) 49 (1977).

[33]King, *Separation Processes*, McGraw-Hill, New York, 1971; Treybal, *Solvent Extraction*, 2d ed., McGraw-Hill, New York, 1963; Hanson (ed.), *Recent Advances in Liquid-Liquid Extraction*, Pergamon, Oxford, 1971.

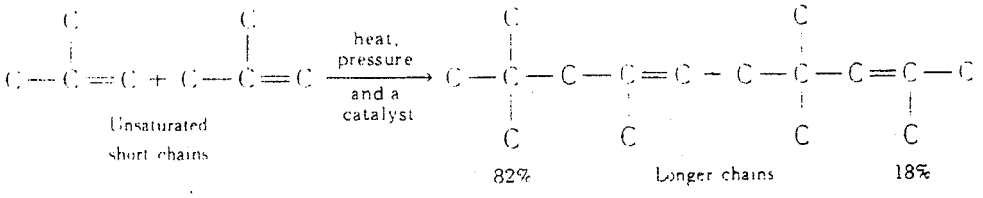
[34]Novel Solvent Recovery Enhances Residuum Upgrading, *Chem. Eng.* 88 (24) 69 (1981).

CONVERSION PROCESSES.[35] About 70 percent of the U.S. crude processed is subjected to conversion processing; both carbonium ion and free radical mechanisms occur. The presence of catalysts, the temperature, and pressure determine which type predominates. The following are examples of the more important basic reactions which occur:

1. ***Cracking, or pyrolysis*** (Figs. 37.9 to 37.12). The breaking down of large hydrocarbon molecules into smaller molecules by heat or catalytic action. Zeolite catalysts are common; other types are also used.

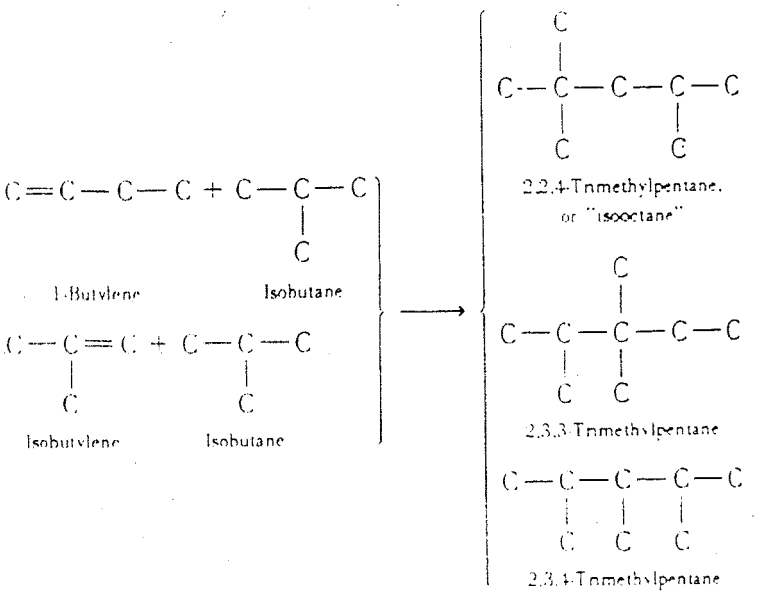
$$\underset{\text{Heavy gas oil}}{C_7H_{15}\cdot C_{15}H_{30}\cdot C_7H_{15}} \rightarrow \underset{\text{Gasoline}}{C_7H_{16}} + \underset{\text{Gasoline (antiknock)}}{C_6H_{12}{:}CH_2} + \underset{\text{Recycle stock}}{C_{14}H_{28}{:}CH_2}$$

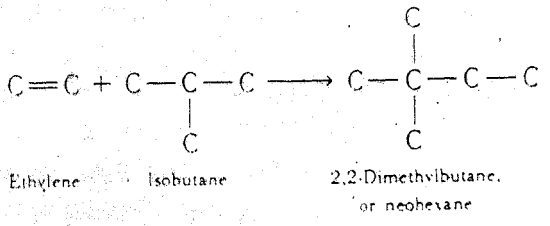
2. ***Polymerization.*** The linking of similar molecules; the joining together of light olefins.



3. ***Alkylation*** (Fig. 37.13). The union of an olefin with an aromatic or paraffinic hydrocarbon.

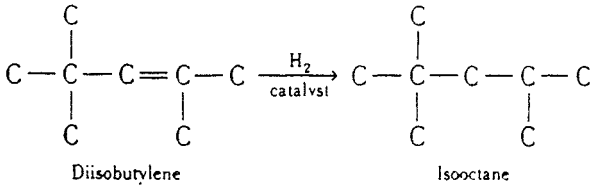
Unsaturated + isosaturated $\xrightarrow{\text{catalyst}}$ saturated branched chain, e.g., catalytic alkylation:





[35] 1982 Refining Handbook, *Hydrocarbon Process.* 61 (9) 101 (1982).

4. ***Hydrogenation.*** The addition of hydrogen to an olefin.



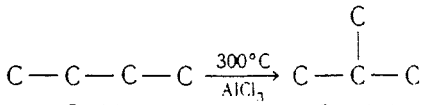
Diisobutylene Isooctane

5. ***Hydrocracking***

$$C_7H_{15}\cdot C_{15}H_{30}\cdot C_7H_{15} + H_2 \longrightarrow \underset{\text{Straight-chain}}{C_7H_{16}} + \underset{\text{Branched-chain gasoline}}{C_7H_{16}} + \underset{\text{Recycle stock}}{C_{15}H_{32}} \text{ (no unsaturates formed)}$$

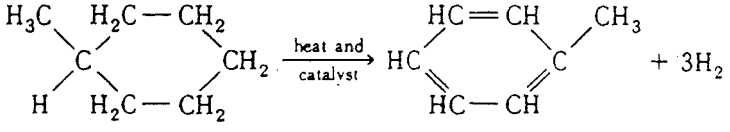
Heavy gas oil

6. ***Isomerization.*** Alteration of the arrangement of the atoms in a molecule without changing the number of atoms.

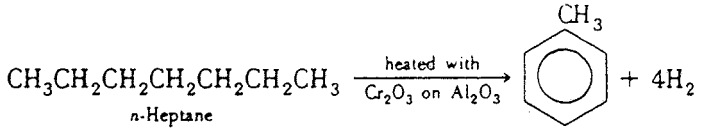


Straight chain Branched chain

7. ***Reforming, or aromatization.*** The conversion of naphthas to obtain products of higher octane number. Similar to cracking, but more volatile charge stocks are used. Catalysts usually contain rhenium, platinum, or chromium.



Methylcyclohexane Toluene



n-Heptane Toluene

8. ***Esterification and hydration*** (Chap. 38).

$$C_2H_4 + H_2SO_4 \rightarrow C_2H_5O\cdot HO\cdot SO_2 + (C_2H_5O)_2\cdot SO_2$$
$$C_2H_5O\cdot HO\cdot SO_2 + (C_2H_5)_2O\cdot SO_2 + H_2O \rightarrow H_2SO_4 \text{ dil.} + C_2H_5OH + C_2H_5OC_2H_5$$

CRACKING, OR PYROLYSIS.[36] When sufficient heat, preferably in the presence of a catalyst, is applied to a paraffin hydrocarbon, it breaks into two (or more) fragments, and one of them is always an olefin. The size of the fragments produced always includes all the possibilities, so the product will be a mixture. A significant amount of polymerization of the smaller molecules always occurs and some carbon is formed. The equations which follow are from Nelson[37] and are simplified examples, for cleavage may occur at any C—C bond.

[36]ECT, 3d ed., vol. 17, 1982, p. 206.

Charge stock $C_7H_{15} \cdot C_{15}H_{30} \cdot C_7H_{15}$
(Heavy gas oil)

↓

Cracked stock $C_7H_{16} + C_{14}H_{28}{:}CH_2 + C_6H_{12}{:}CH_2$
(Gasoline + Recycle stock + Gasoline (antiknock))

↓

More cracking $C_2H_6 + (C_4H_8{:}CH_2 + C_8H_{18} + C_6H_{12}{:}CH_2)$ (Gas; Gasoline)
$+ CH_2{:}CH \cdot CH{:}CH \cdot CH_3 - C_2H_4$
(Gum-forming materials; Gas)

↓

Polymerization $C_2H_6 + (C_4H_8{:}CH_2 + C_8H_{18}) + C_{12}H_{22} + C_2H_4$
(Gas; Tar or recycle; Gas)

All cracking reactions are endothermic and the energy involved is usually high. The reactions are sufficiently complicated to make accurate calculation of reaction heats difficult to impossible.

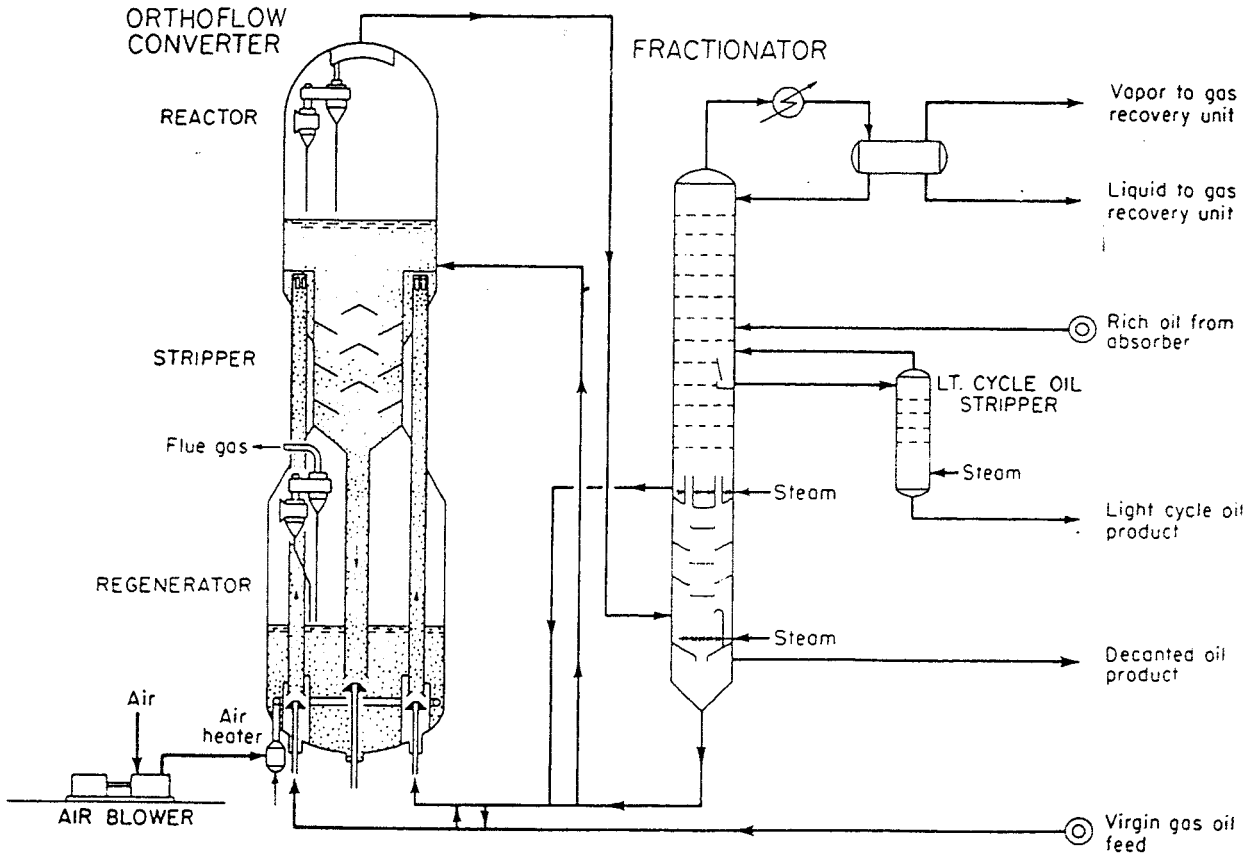
Cracking conserves fuel because it makes possible efficient use of virtually all the crude. Gas oil was the original cracking stock. Present techniques make possible cracking of refinery naphthas and even of quite heavy stocks and reduced crude. Essentially all present-day cracking is done in the presence of catalysts.

Catalytic cracking was first brought about by using fixed beds of catalyst. Such beds can function for only a few minutes before carbon deposition reduces or stops catalytic activity. The bed must then be regenerated by burning the carbon off under carefully controlled conditions to avoid sintering of the catalyst and recover the valuable heat of its combustion. Such units proved to be cumbersome and were soon replaced by several variants. First the catalyst was moved mechanically; later the fluid catalytic process took over. Engineers noted that, with proper agitation, a finely divided suspension of solid in gas would flow like a liquid and could be handled with liquid pumps and exchange heat in double-pipe exchangers without settling. Because gas is light and the solid is heavy, the mixture tends to possess the properties of the solid, so the high specific heat makes temperature control remarkably precise. Utilizing these principles enabled catalyst-vapor contact to be handled very well, temperature control to be greatly improved, and by moving the catalyst about as a fluid, it no longer was necessary to confine it to a bed-in-place. Cracking and regeneration took place in two units and the solids were separated from the vapors and flue gases by using cyclone separators. All cycles are continuous (Figs. 37.9 and 37.10).

The M. W. Kellogg Orthoflow and the newer Ultra-Orthoflow fluid cracking units[38] are typical of units carrying out reaction, catalyst stripping, regeneration, and catalyst circulation in a single converter (Figs. 37.9 and 37.10). The reactor is mounted above the regenerator and the catalyst stripping section is located in-between, so the stripper supports the reactor. The Orthoflow design provides straight-line flow of the catalyst between the converter compartments, virtually eliminating the erosion normally encountered in pipe bends. Within the converter, the powdered synthetic catalyst is maintained in a fluidized bed by controlled

[37]Nelson, op. cit.

[38]*Hydrocarbon Process.* **58** (9) 131 (1979); **61** (9) 101 (1982).



Operating conditions can be described as follows:

	USUAL RANGES	TYPICAL CONDITIONS
Reaction temperature C°	475–550	496
Reaction pressure, kPa	170–310	163
Regenerator temperature, C°	675–760	621
Regenerator pressure, kPa	204–340	211
Catalyst/oil ratio	6–20	6.2
Space velocity, wt/wt-h	1.0–16.0	2.4

Yields from gasoline cracking can be varied within limits to suit a refiner's special local conditions. Typical yields from a Kellogg Orthoflow unit operating at a comparatively high conversion are:

Charge density	0.893	C_4 + gasoline, vol %	67.4
Throughput ratio	1.95	Light cycle oil, vol %	21.0
Conversion, vol %	76.0	Fractionator bottoms, vol %	3.0
C_2 and lighter, wt %	4.0	Coke, wt %	10.0
C_3, vol %	9.7		

Typical requirements,* unit per cubic meter of fresh feed:

Electricity, MJ	136	Water, boiler feed, m^3	0.286
Steam (generated), kg	(14.9)	Catalyst consumption, kg	0.09–0.18
Water, cooling (22° rise), m^3	7.55		

**Excludes recovery plant. Using electric drive on the air blower. There is a net production of steam. Also 39 MJ of heat is available for use in the recovery plant.*

Fig. 37.9. Orthoflow catalytic cracking converter and adjuncts. Stippled areas represent fresh or regenerated catalyst. *(M. W. Kellogg Co.)*

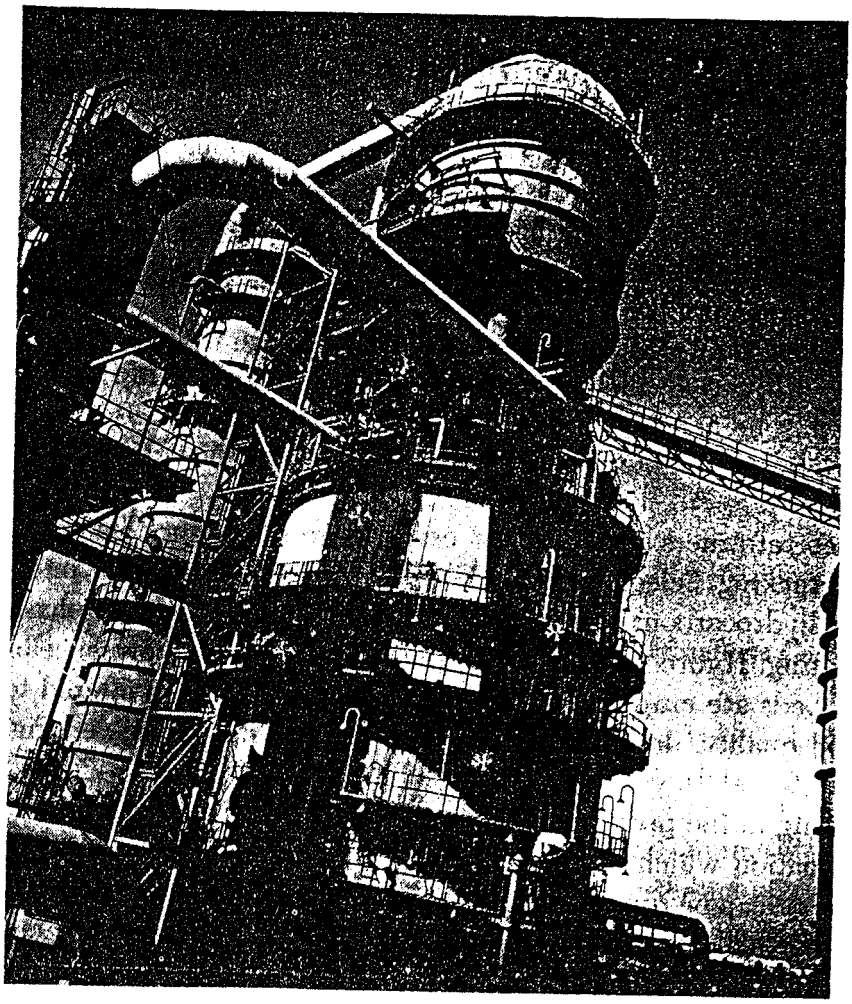


Fig. 37.10. Orthoflow catalytic cracker. *(M. W. Kellogg Co.)*

ing vapors. Circulation is maintained by having different concentrations in the catalyst circulation lines.

During operation, the hot catalyst from the regenerator enters the feed-regenerated catalyst risers through plug valves. Feed and dispersion streams are fed simultaneously through the hollow stem of the valves and mix with the catalyst. Heat from the regulated amount of hot catalyst vaporizes the oil and raises it to the required reaction temperature. As the oil and catalyst pass up the risers, the cracking reaction takes place. The risers terminate in the reactor, where additional cracking takes place, either in a dense bed or a disperse phase. The cracked products, steam, and inerts enter a disengaging space, from which the catalyst falls back into the bed. Reactor effluent passes upward through cyclones for separation of the catalyst from reactor overhead vapors. Spent catalyst from the cracking reaction leaves the reactor and passes through the stripper, where it is steam-stripped to remove cracked products and cycle oil trapped by the down-flowing catalyst. The stripper catalyst then falls, in a dense phase, down the spent-catalyst standpipes, through plug valves, and into the regenerator bed. Here coke laid down on the catalyst during reaction is burned off, using air. Combustion flue gas passes upward from the fluid bed through a disengaging zone and then through several stages of cyclones (usually two to three stages). The flue gas may be vented to the atmosphere or sent to CO boilers (where the CO contained in the flue gas is burned) for the generation of high-pressure steam.

Since the reactor effluent is a complex mixture of inerts, gas, butanes, gasoline, and cycle-oil stocks, it must be separated into the desired product streams. Reactor overhead vapors are separated in the catalytic fractionator. The vapors leaving the catalytic fractionator overhead

reflux drum contain valuable gasoline components, and the raw unstabilized (i.e., high vapor pressure) gasoline contains undesirable light hydrocarbons. The recovery, separation, and purification of these light ends and gasoline are accomplished in a gas-recovery plant which utilizes gas compression and recovery equipment in an absorption-and-fractionation system.

A valuable heating-oil product called light cycle oil is condensed in the section immediately above the heavy cycle-oil section of the tower. The light cycle oil is generally drawn from the tower as a side stream, stripped with steam, and sent to storage A rich oil stream is returned to the catalytic fractionation from the gas plant, where it has served as a sponge-oil medium to recover valuable hydrocarbons which otherwise would be lost to fuel gas.

This *fluid catalytic process* contributes a valuable principle to the chemical industry. The use of a large amount of turbulent solid capable of absorbing much heat in the reaction mass greatly reduces temperature variations and hot spots. If no catalytic action is desired, an inert, powdered solid may be used.

A wide variety of bed-in-place reformers and fluid-bed crackers go under such names as Isocracking, Ultracracking, Unicracking, Selectoforming, Ultracat, etc. The increasing interest in products from the heavier hydrocarbons at the "bottom of the barrel" places emphasis on hydrocracking and hydrotreating. Hydrocracking[39] is strong processing in the presence of hydrogen. Both fixed and fluid beds are employed. Light and heavy gas oils are altered to distillable light products of good quality, desulfured, demetallized, and stabilized. See Fig. 37.11.

Hydrotreating is mild processing in the presence of hydrogen, and desulfurizes, improves color, reduces metallic contamination which is destructive to cracking catalysts, improves storage stability, saturates olefins, or can be run selectively to saturate only diolefins. Improvements in specialty products are particularly marked.

REFORMING. Reforming means just what the name implies—forming new molecules of a size similar to the original ones. Because the octanes of straight run gasolines, naphthas, and

[39]Menzies, Silva, and Denis, Hydrocracking without Catalysis Upgrades Heavy Oil, *Chem Eng.* 88 (4) 46 (1981); Details of Dynacracking Process Revealed, *Chem. Eng. News.* 58 (30) 24 (1980); Berry, A Heavy, Sour Taste for Crude Oil Refiners, *Chem. Eng.* 87 (10) 96 (1980).

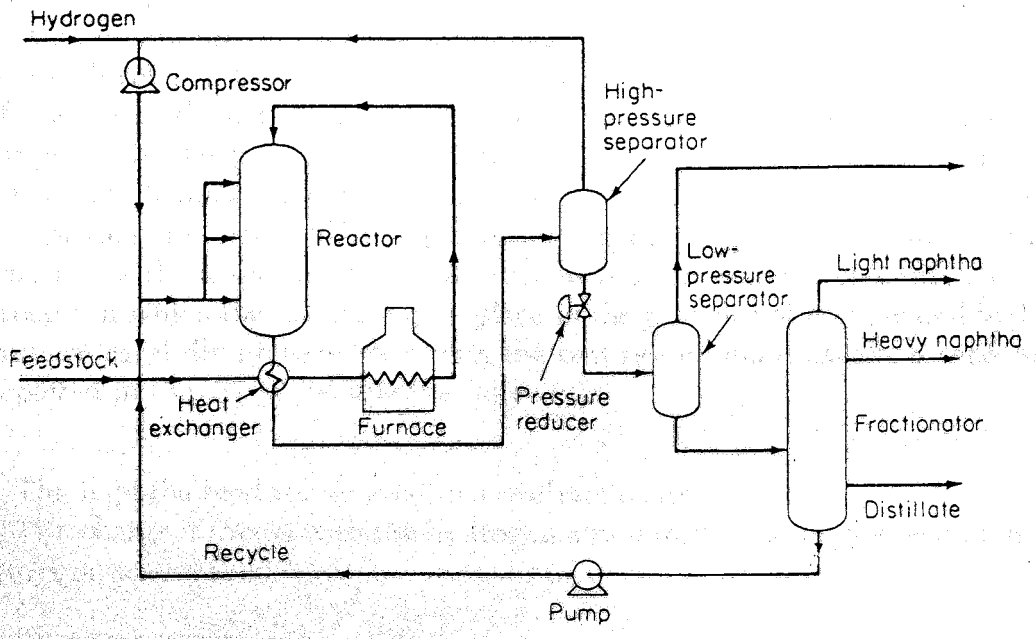


Fig. 37.11 Hydrocracking.

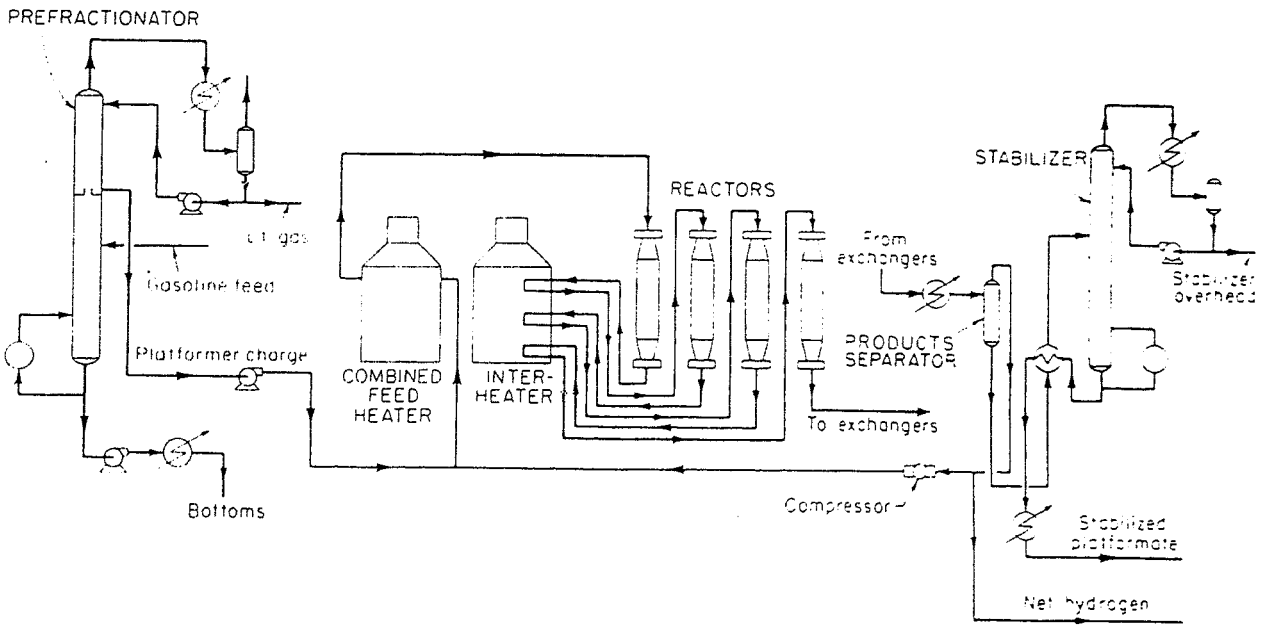


Fig. 37.12. Flowchart for platforming. *(Universal Oil Products Co.)*

natural gasolines are low, these fractions are subjected to a high-temperature catalytic treatment, frequently in the presence of hydrogen, designed to preserve their present molecular size, but convert them into branched-chain and aromatic compounds with high antiknock ratings. This expensive process has become essential since the Environmental Protection Agency adopted the phase-out rules for lead. Without lead, enough high-octane motor fuel simply cannot be made without reforming—a combination of isomerization and cracking.

Catalytic Reforming. This involves the conversion of other hydrocarbons into aromatic compounds. Because of the high octane rating of aromatic compounds and the proved practicability of the process, catalytic reforming has now almost completely replaced thermal reforming. Catalysts such as platinum on alumina or silica-alumina and chromia on alumina are used. The Universal Oil Products Co. showed that these expensive catalysts could be used by reducing catalyst losses. Rhenium catalysts have come into use.

Another example of catalytic reforming is the *platforming* process[40] depicted in Fig. 37.12. It was developed by the Universal Oil Products Co. as an "economical commercial method of upgrading the octane ratings of straight run, natural and thermally cracked gasolines, and for producing large quantities of benzene, toluene, xylenes, and other aromatic hydrocarbons for use in chemical manufacture and in aviation fuel." The name comes from the fact that this process uses a fixed-bed Al_2O_3 catalyst containing 0.25% platinum. This catalyst has a long life without regeneration. The process is as an example of a specialized hydroforming process in which the reactions take place in the presence of recirculated hydrogen. The feed must be carefully prepared to obtain the best results and is usually a naphtha cut. The steps depicted in Fig. 37.12 include the following:

The naphtha feed is prepared in a prefractionator.

The charge is mixed with the hydrogen and introduced into the feed preheater, where the temperature is raised.

[40] *Oil Gas J.* **70** (21) 52 (1972); Continuous Regenerator Smooths Naphtha Reforming, *Chem. Eng.* **79** (18) 80 (1972).

The hot-feed naphtha vapors are conducted with recycle hydrogen through the four catalyst-containing reactors in series with an interheating for each reactor. The temperature is 150 to 510°C and the pressure 1500 to 7000 kPa.

The reactions that take place are essentially as follows:

1. Isomerization of alkycyclopentanes to cyclohexanes.
2. Dehydrogenation of cyclohexanes to aromatics.
3. Dehydrocyclization of paraffins to aromatics.
4. Hydrocracking of paraffins and naphthenes.
5. Hydrogenation of olefins.
6. Isomerization of paraffins.
7. Desulfurization.

After the reactor, the products are cooled in heat interchangers. From the exchanger 90% hydrogen is obtained, compressed, and recycled. The main product is fractionated after the temperature is reduced to the proper point in heat exchangers and conducted into a fractionating column or stabilizer, the overhead from which may be used as fuel.

The product is stabilized *platformate,* which may be used as a high-octane gasoline or further fractionated into its constituents, e.g., to furnish benzene, toluene, and xylenes.

COKING. Lighter oils can be produced from very heavy ones by a solely thermal cracking process. The feed is usually a vacuum residue and considerable coke is formed. Delayed or fluid coking processes are used on low value residuals, avoiding catalyst fouling by asphalts which would otherwise make fluid catalytic cracking (FCC) difficult.

Another process known as Flexicoking takes the coke made and converts it into clean fuel gas by gasifying it with steam and air or oxygen.

Viscosity breaking is another thermal cracking process which is used to reduce the viscosity of heavy fuel oil.

Oxidation.[41] Oxidation-conversion as applied to petroleum gives more trouble than useful products, forming as it does gums and resins that interfere with the employment of gasolines, particularly those which contain unsaturated compounds. However, some serviceable products are obtained from petroleum by oxidation, e.g., formaldehyde by restricted oxidation of methanol and by restricted oxidation of natural gas. Much study is also being directed toward making fatty acids[42] from paraffins and even food products. Blown asphalt is made by oxidation. Synthesis gas is made by partial oxidation of hydrocarbons,[43] and from it a wide variety of products are made including ammonia, methanol, and oxo-alcohols.

Polymerization.[44] Polymerization processes convert by-product hydrocarbon gases produced in cracking into liquid hydrocarbons suitable for use as high-octane motor and aviation

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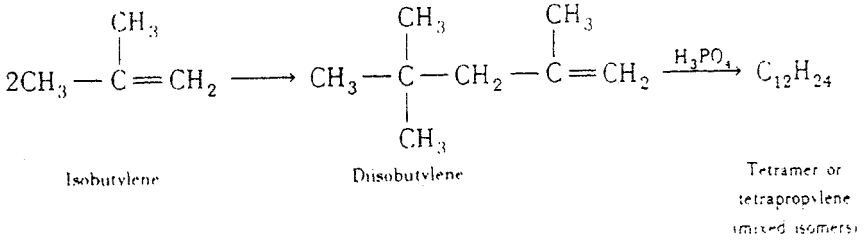
[41]Weismantel and Ricci, Partial Oxidation in Comeback, *Chem. Eng.* 86 (21) 57 (1974).

[42]Pardun and Kuchinka, Reaction Rates in the Liquid-Phase Oxidation of Paraffins, *Petrol. Refiner* 22 (11) 140 (1943); Partial Oxidation for Syngas and Fuel, *Hydrocarbon Process.* 53 (12) (1974).

[43]Marsh and Herbort, Synthesis Gas by Steam Reforming of Natural Gas, *Hydrocarbon Process.* 61 (6) 101 (1982); 61 (3) 92 (1982).

[44]Polygas Spells Relief from Alkylation Ills, *Chem. Eng.* 87 (12) 77 (1980).

fuels and for petrochemicals. To combine olefinic gases by polymerization to form heavier fractions, the combining fractions must be unsaturated. Hydrocarbon gases from cracking stills, particularly olefins, have been the major feedstock of polymerization. The following equation is typical of polymerization reactions. Propylene, normal butylene, and isobutylene are the olefins usually polymerized in the vapor phase.



Vapor-phase cracking produces considerable quantities of unsaturated gases suitable as feedstocks for polymerization units.

Catalytic polymerization is practical on both a large and a small scale and is adaptable to combination with reforming to increase the quality of the gasoline (Fig. 37.12). Gasoline produced by polymerization contains a smog-producing olefinic bond. Polymer oligomers are widely used to make detergents. Since the middle and late 1950s, polymerization has been supplemented by alkylation as a method of conversion of light (C_3 and C_4 gases to gasoline fractions.

Alkylation.[45] Alkylation processes are exothermic and are fundamentally similar to polymerization; they differ in that only part of the charging stock need be unsaturated. As a result, the alkylate product contains no olefins and has a higher octane rating. These methods are based on the reactivity of the tertiary carbon of the isobutane with olefins, such as propylene, butylenes, and amylenes. The product *alkylate* is a mixture of saturated, stable isoparaffins distilling in the gasoline range, which becomes a most desirable component of many high-octane gasolines.

Alkylation is accomplished on a commercial scale with two catalysts: hydrogen fluoride and sulfuric acid. Alkylation with liquid hydrogen fluoride is illustrated by the flowchart in Fig. 37.13. Here the acid can be used repeatedly, and there is no acid-disposal problem. The acid hydrocarbon ratio in the contactor is 2:1. The temperature range, from 15 to 35°C, is cheaply maintained, since no refrigeration is necessary. The simplified reaction is as given for the conversion process of alkylation, with a two- to threefold excess of isobutane over the butylenes to minimize realkylation of the primary alkylate. The anhydrous hydrofluoric acid, when dirty, is easily regenerated by distillation from heavy alkylate. Sufficient pressure is required on the system to keep the reactants in the liquid phase. Corrosion is low, and the separated isobutane is recycled. Also, alkylation results from the combination of an olefin or alkyl halide with an aromatic hydrocarbon (Chap. 38). The *Bergius process*, originated in Germany for the production of oils by hydrogenation of coal, finds no use in the United States at present. It has been tried in this country only on a semiworks scale. The synthesis of motor fuel from carbon monoxide and hydrogen is a hydrogenation process which was industrialized in Germany as the Fischer-Tropsch process[46] to make Synthol. The largest Fischer-

[45]Groggins, 5th ed., op. cit., p. 894 ff.

[46]Groggins, op. cit., p. 564; Kellogg, Synthol Process, *Petrol. Refiner*, November 1963, p. 42 (flowchart and description).

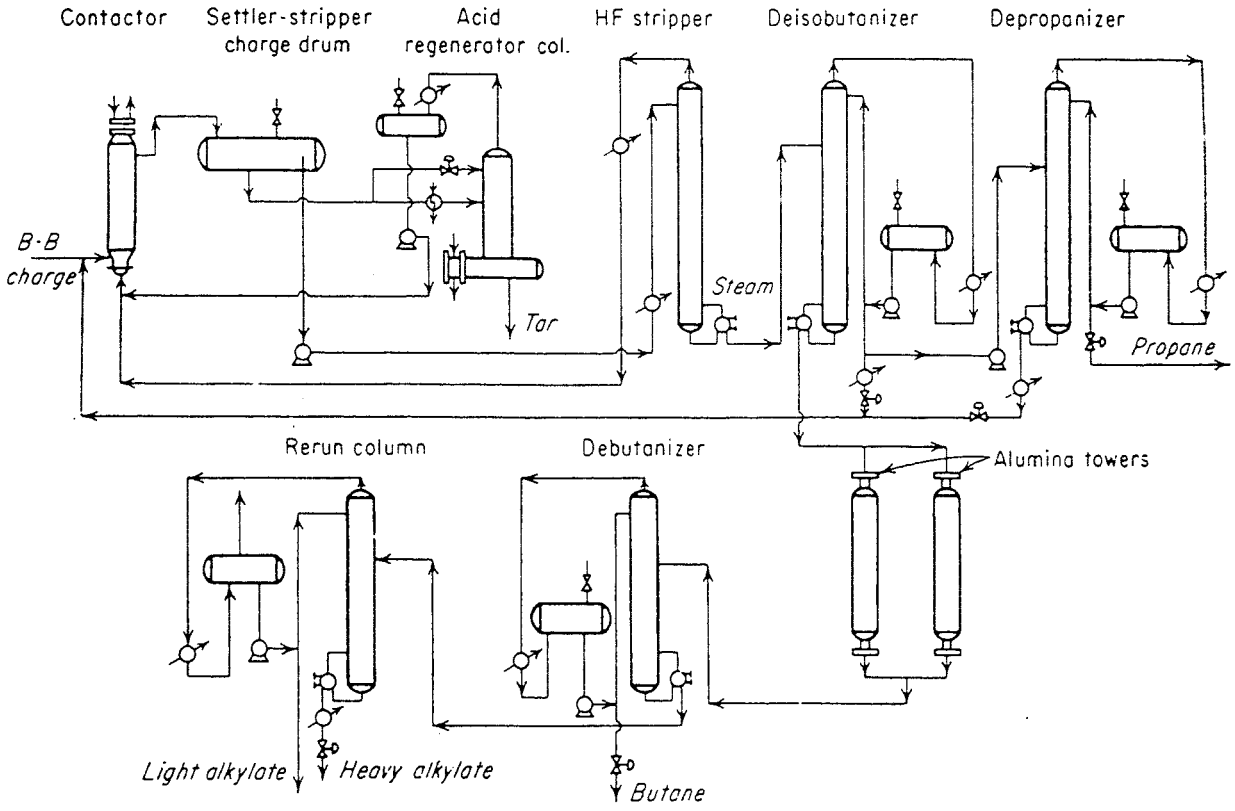


Fig. 37.13. Flowchart for HF alkylation. *(Universal Oil Products Co.)*

Tropsch plant is in South Africa, built by the M. W. Kellogg Co. This plant[47] has run successfully for over 25 years, producing motor fuels and other products for a petroleum-short country.

Isomerization.[48] This conversion process has become of the utmost importance in furnishing the isobutane needed for making alkylate as a basis for aviation gasoline (see alkylation). The reaction may be formulated:

$$\underset{n\text{-Butane}}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3} \longrightarrow \underset{\text{Isobutane}}{CH_3 \cdot \overset{CH_3}{\overset{|}{C}}H \cdot CH_3}$$

CHEMICAL TREATMENT. Some type of chemical treatment to remove or alter the impurities in petroleum products is usually necessary to produce marketable material. Depending upon the particular treatment used, one or more of the following purposes are achieved:

1. Improvement of color.
2. Improvement of odor.
3. Removal of sulfur compounds.
4. Removal of gums, resins, and asphaltic materials.

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[47]Dry, Sasol's Fischer-Tropsch Experience, *Hydrocarbon Process.* 61 (18) 121 (1982); Dry, The Sasol Route to fuels, *CHEMTECH* 12 (12) 744 (1982).

[48]Egloff, Hulla, and Komarewsky, *Isomerization of Pure Hydrocarbons*, Reinhold, New York, 1942; Liquid-Phase Isomerization, *Petrol. Refiner* 23 (2) 61 (1944).

5. Improvement of stability to light and air.
6. Improved susceptibility to additives.

Of these, removal of sulfur[49] and improvement of stability are the factors usually governing the treatment employed. With the discovery that the use of catalytic converters causes the emission of sulfuric acid vapors from automobile exhausts, pressure to remove or reduce sulfur in motor fuel has developed. Sulfur may be reduced by (1) hydrogenation (which also removes metals and nitrogen), (2) treatment with caustic soda, (3) treatment with caustic soda plus a catalyst (Merox), and (4) treatment with ethanolamines.

Several processes are available for the alteration of objectionable sulfur and the consequent improvement in odor. The *doctor treatment* was the original method of "doctoring" the oil to reduce the odor and utilized sodium plumbite to convert mercaptans to less objectionable disulfides. A number of processes are now aimed at removing sulfur-containing compounds. Hydrogen treatment reduces the sulfur in heavy fractions and resids. Hydrogen or hydrogen-donor liquids and a catalyst are used to treat lighter distillates, removing nitrogen, sulfur, and some metallic contaminants as well. Extraction with caustic or proprietary solutions (usually oxygen-regenerable) is frequently used on light distillates.

It is now common practice to add antioxidants to prevent the formation of gums, rather than to remove them chemically. Among the *antigumming* materials used are α-naphthol, substituted catechols, cresols, benzyl-*p*-aminophenols, and certain wood-tar and coal-tar fractions.

WASTE TREATMENT. Sulfur compounds in stack gases and a variety of extracts and wastes found in refinery waste waters must be disposed of. Treatment of these two types of wastes to give acceptable environmental control now approaches the size and cost of the remainder of the refinery.

Research. The petroleum industry has been characterized by continuous improvement based upon research and a willingness to replace antiquated equipment or old processes by more modern ones. This development went through two phases. In the first phase, the *unit operations*, distillation, heat transfer, fluid flow, and the like, were subjected to accurate study and experimentation; these operations could be carried out with greater efficiency and consequently less cost. However, the second phase of research was the study of chemical changes involving petroleum raw materials and petroleum products.

Most current research seeks new and better catalysts, or improvements in old processes. Little basic research is being done. Very expensive developmental research continues to be done on other sources of oil supply. Shale oil mining and retorting, oil sands recovery procedures, coal liquefaction, biomass conversion to fuel, and gasohol from grain are examples of fields being actively studied now.

To maintain a competitive and well-rounded position many petroleum compounds must be chemically altered to obtain products of greater usefulness or value. Each year shows a higher percentage of petroleum sales from the action of chemical change on petroleum raw materials. Indeed, the petroleum industry has become the most important source of cheap raw materials for the entire chemical industry. Such chemical change will be more marked in the future than it has been in the past. The present sound technical position has come about as a result of technical research protected by patents, but proportionately less money is being spent on research than in the past.

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[49]A Sulfur in Gasoline Scare? *Chem. Eng.*, 81 (26), 74 (1974); Ranney, *Desulfurization of Petroleum*, Noyes, Park Ridge, N.J., 1975.

Other Products from Petroleum. Because petroleum contains so many constituents and is reactive in so many different ways, new products are constantly being sought and found. After conversion to methanol, it is possible to grow single-cell protein suitable for human and animal food. Bacteria can also grow on methane and other hydrocarbons.[50] Several large plants have been built in Europe and Asia, but acceptance of the products has been disappointing.

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[50]Skinner, Single Cell Protein Moves toward Market, *Chem. Eng. News* 53 (18) 24 (1974); Harrison, Making Protein from Methane, *CHEMTECH* 6 (9) 570 (1976).

Chapter 5

Petrochemicals

Just a few years back, it was easy to define petrochemicals—they were relatively pure, identifiable substances derived from petroleum and used in the chemical trade. Now conversion processes are often built in as part of separation processes making original products more complex; oil companies are entering the chemical business; chemical companies are entering the oil business; and the whole group is expanding greatly, so most organic chemical substances could be considered petrochemicals.

Most processes for separating individual species from petroleum involve using refined engineering methods, with distillation and selective adsorption the most important. Once separated, however, most materials then undergo chemical conversion into more desirable products. Alkylations involving propenes and butenes yield C_6 to C_8 hydrocarbons for high-octane gasoline. Propylene becomes polypropylene, propylamines, or propylene glycol and ethers. Every phase of organic chemistry has been touched and altered by the availability of petrochemicals. Even the field of aromatics, once the sole province of coal-derived chemicals, now derives over 98 percent of its raw materials from petroleum. The major production plants developed along the Gulf of Mexico coast, because the needed raw materials and water transport are there, but increasingly plants are spreading out into consuming areas. In addition to the usual organics, by-product sulfur has become a dominant factor in the market.

Oil companies have traditionally made their profits more from production than from product sales. Their thinking has been geared to high-sales low-profit operations in the refining business. There has also been great reluctance to make long-term commitments. This, of course, is the direct opposite of the chemical industry's usual long-time commitments to comparatively low-volume high-profit operations. The growth of the enormous plastic industries and other very large scale organic chemicals (ethylene glycol, methanol, ethanolamines, etc.) has brought the viewpoints of the two industries much closer together. At first, chemical companies bought simple raw materials of the required purity directly from the oil companies. then oil and chemical companies formed joint ventures; now integration from underground oil to finished product is taking place with both oil and chemical companies becoming indistinguishable. Most major oil companies now have petrochemical departments which are frequently separate from their refining departments. The manufacture of intermediates is frequently more profitable than simple raw material supply.

HISTORICAL. The first organic chemical made on a large scale from a petroleum base was isopropyl alcohol (isopropanol), first produced by Standard Oil of New Jersey in 1920. Depending on the definition and the number of conversions permitted by the statistician, certainly over 3000 individual petrochemicals enter into commerce. Over one hundred are presented in this chapter and other parts of the book. This business changes very rapidly as new processes simplify old ones and price changes make usability vary; so many historically important processes have become economically or technologically obsolete. Within the past

few decades, processes for making ammonia, ethyl alcohol, acetic acid, acetone, glycerin, acetylene, and other major chemicals have been revised and are now almost totally petroleum-derived.

RESEARCH. The birth and growth of petrochemicals has been one of the fabulous stories connected with modern chemical and chemical engineering research. Petroleum companies were uninterested in chemical production, but gave the industry a great boost by selling their off-gas to chemical companies at its fuel value. Cracking furnaces put reactive olefins in these gases, which chemical companies quickly developed into petrochemicals. Some oil companies, for example, Shell and Standard Oil of New Jersey (now Exxon), became involved in chemical production much earlier than others.

ECONOMICS AND USES. By 1925, Standard Oil of New Jersey was making 75 t/year of isopropyl alcohol, and the emergence of the petrochemical industry was established in many minds.[1] Currently, well over 80 percent of all organic chemicals are petrochemicals. The percentage continues to increase despite a nearly ten to one increase in the price of raw material. The classes of end use for petrochemical products are listed in Table 38.1. Companies continue to expend large sums on capital improvements needed for petrochemicals, although the industry is currently having a severe sales slump. Prescott[1a] has estimated and tabulated the petrochemical growth of oil and chemical companies since 1974. He predicts a large and profitable growth of the industry, particularly in polymers and agrichemicals. Like other businesses, growth has been delayed by the current recession. Hatch and Matar[2] have made an excellent summary of the technology of the industry.

FEEDSTOCKS. The most basic raw materials (Table 38.2) supplied by petroleum refineries or natural gas companies are LPG, natural gas, gas from cracking operations, liquid distillate (C_4 to C_6), distillate from special cracking processes, and selected or isomerized cyclic fractions for aromatics. Most of these substances are of high value for fuel use, and attention is

[1] t = 1000 kg.

[1a]Prescott, Oil Giants Gear Up Petrochemicals Capacity, *Chem. Eng.* 82 (7) 56 (1975).

[2]Hatch and Matar, *From Hydrocarbons to Petrochemicals*, Gulf, Houston Tex, 1981.

Table 38.1 End Products of the Petrochemical Industry with Reference Chapter Number

Product	Chap.	Product	Chap.
Adhesives	25	Industrial gases	7
Agrichemicals	26	Lubricants and additives	37
Alcohols	38	Medicinal products	40
Ammonia	18	Nitrogen industries	18
Antifreeze and antiknock	38	Paints, varnishes, etc.	25
Detergents	29	Plastics, polymers, and plasticizers	34
Dyes, lakes, and toners	39	Rubber, rubber chemicals	36
Explosives	22	Solvents	38
Fertilizers and pesticides	26	Sulfur and sulfuric acid	19
Flavors and perfumes	27	Surface coatings	24
Flotation agents	38	Synthetic fibers	35
Food additives	26	Synthetic motor fuels	37
Industrial carbon	8		

Table 38.2 Primary Precursors: Petroleum-Petrochemical Complex

Raw Materials by Distillation	Precursors (basic chemicals) by Conversion	Intermediates by Conversion	Finished Products by Conversion
Paraffins and cyclics	Olefins, diolefins, acetylene, aromatics	Various inorganics and organics	Inorganics and organics
Natural gas			Carbon black
Sulfides	H_2S	S, H_2S	H_2SO_4
Hydrogen		Synthesis gas	NH_3
Methane			Methanol
			Formaldehyde
Refinery gases	Acetylene	Acetic acid	Acetates
	Isobutene	Acetic anhydride	Fibers
Ethane°	Ethylene	Isoprene	Rubber
Propane°	Propylene	Ethylene oxide, etc.	Rubber and fiber
n-Butane°	*n*-Butenes	Butadiene	Rubber
Hexane			
Heptanes			
Refinery naphthas			
Naphthenes	Cyclopentadiene	Adipic acid	Fibers
Benzene	Toluene	Ethylbenzene	Styrene
		Styrene	Rubber
		Cumene	Phenol, acetone
		Alkylbenzene	
		Cyclohexane	Nylons
Toluene	Toluene	Phenol	Plastics
		Benzoic acid	Phenol
Xylenes	*o*-, *m*-, *p*-Xylene, toluene	Phthalic anhydride	Plastics
Methyl naphthanes	Naphthalene		

°From LPG and refinery cracked gas.

NOTE: Aromatics are also obtained by chemical conversions (demethylation, etc.).

increasingly turning to the use of less desirable high-molecular-weight feedstocks. To make this source attractive, cost must be less than or the same as the present sources of the low-molecular-weight precursors produced. Coking processes, hydrocracking, and high severity catalytic cracking appear to be the more attractive routes to explore.

Mixtures are usually separated into their components at the petroleum refineries, then chemically converted into reactive precursors before being sold to outside processors or converted into salable chemicals within the plant.

The lower members of the paraffin and olefin series have been the preferred and most economical sources of organic raw material for conversion, so figures and tables are shown concerning the derivations from methane (Fig. 38.1 and Table 38.3), ethylene (Fig. 38.2 and Table 38.4), propylene and butylene (Fig. 38.3 and Table 38.5), and cyclic materials (Fig. 38.4 and Table 38.6). The tonnage of these materials used has increased rapidly for some years, and the number of final products produced has also grown. Presumably, rapid growth will resume as the business climate improves. The manufacture of olefins and aromatics is discussed in Chap. 37 along with some intermediates. Salable products made from these are listed in the various tables and figures of this chapter. The manufacturing procedures for a number of technically important petrochemicals are used to clarify the types of conversion processes discussed in the latter part of the chapter.

As synthetic organic chemistry made new products possible, petrochemicals stood ready to fulfill the demand for raw materials because oil, and particularly natural gas, was available

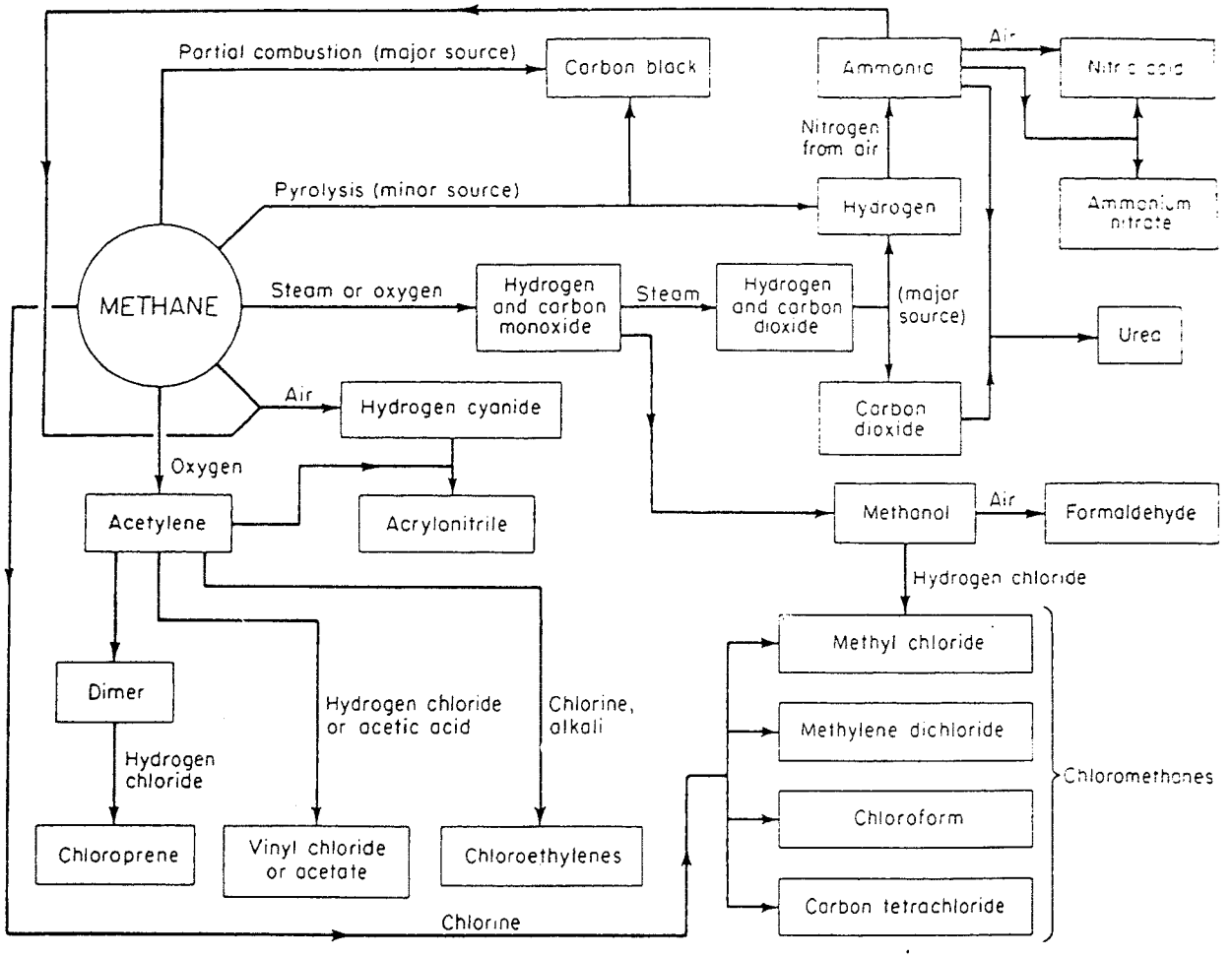

Fig. 38.1. Petrochemicals from methane. *(McGraw-Hill Encyclopedia of Science and Technology, 5th ed., vol. 10, 1982, p. 62.)*

Table 38.3 Petrochemicals from Methane

Basic Derivative	Produced Annually, 10^6 kg (last year reported)*	Uses, percent
Ammonia	17,545	Fertilizer 80, plastics and fibers 10, explosives 5
Carbon black	1,227	Tires 65, other rubber 25, colorant and filler 10
Methanol	3,830	Polymers 50, solvents 10, derivatives (HCHO,CH_3COOH)
Chloromethanes		
CH_3Cl, methyl chloride	177	Silicones 57, tetramethyl lead 19
CH_2Cl_2, methylene chloride	236	Paint remover 30, aerosol propellant 20, degreaser 10
$CHCl_3$, chloroform	183	Fluorocarbons 90
CCl_4, carbon tetrachloride	322	Fluorocarbons 95, degreasing, fumigant, etc. 5
Acetylene	131	VCM 37, 1,4-butanediol 25, V acetate 14, V fluoride, and acetylene black 5
Hydrogen cyanide	227	MMA 58, cyanuric chloride 17, chelating agents 13, NaCN 9

*Usually 1981.

SOURCES: *Chem. Eng. News* and *Chem. Mark. Rep.*

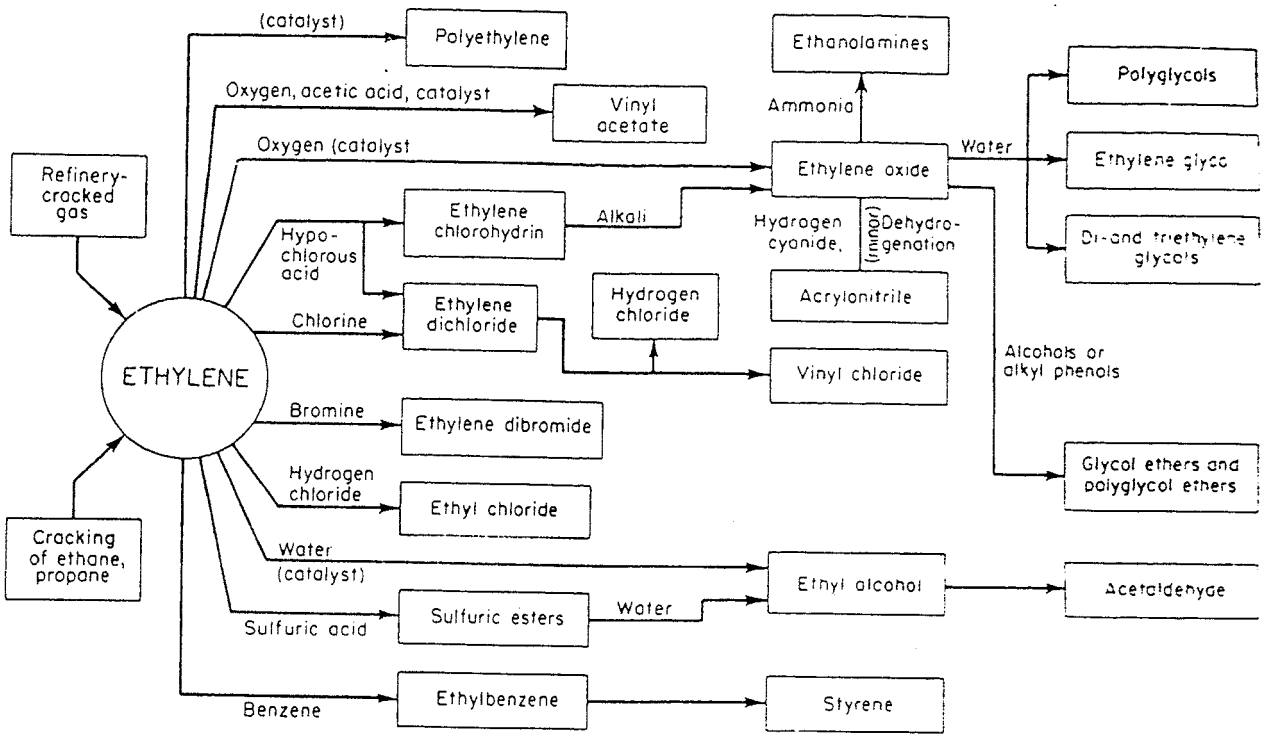

Fig. 38.2. Petrochemicals from ethylene. *(McGraw-Hill Encyclopedia of Science and Technology, 5th ed., vol. 10, 1982, p. 63.)*

Table 38.4 Petrochemicals from Ethylene

Basic Derivative	Produced Annually, 10^6 kg (last year reported)*	Uses, percent
Ethyl benzene	3474	Styrene 99, solvent 1
Ethyl chloride	191	TEL 90, ethyl cellulose and pharmaceuticals 5
Ethylene dichloride	5227	VCM 84, solvent 7
Ethylene glycol	2050	Antifreeze 38, polyester fibers and films 49
Ethylene oxide	2320	Glycol 60, ethoxylates 10, glycol ethers 10
Perchloroethylene	327	Textile cleaning 40, metal cleaning 21, chemical intermediate 6
Polyethylene		
Low density (including LLDPE)	3320	Film, sheet, molding, and extrusion plastic
High density	2186	Film, sheet, molding, and extrusion plastic
Styrene	3182	Polystyrene 52, ABS 9, SBR 7, polyester resins 6, SB latex 6
1,1,1-Trichloroethane	283	Cold cleaning 40, vapor degreasing 22, adhesives 12, aerosols 10, electronics 6

*Usually 1981.

SOURCE: *Chem. Eng. News* and *Chem. Mark. Rep.*

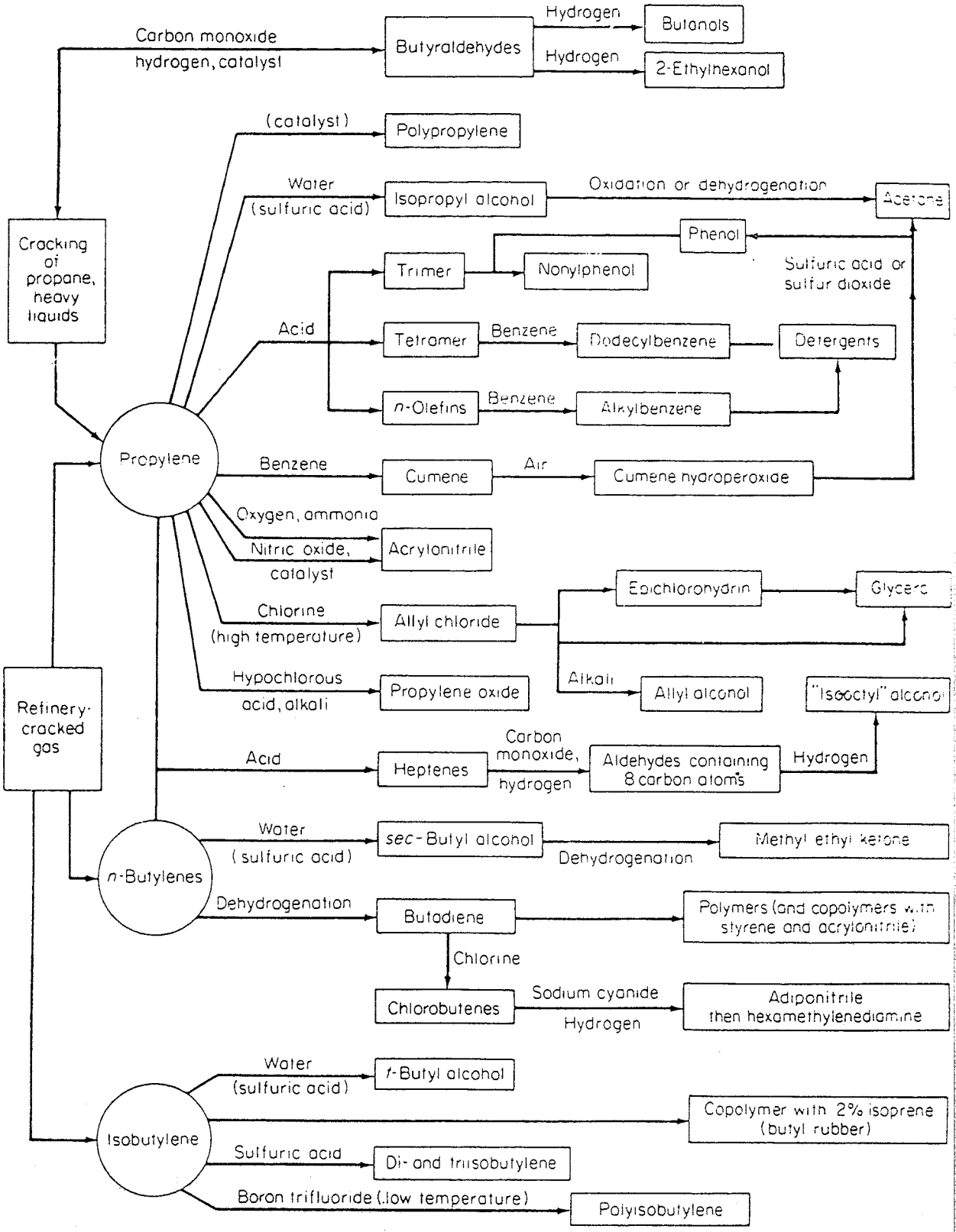

Fig. 38.3. Petrochemicals from propylene and the butylenes. *(McGraw-Hill Encyclopedia of Science and Technology, vol. 10, 1982, p. 65.)*

Table 38.5 Petrochemicals from Propylene and the Butylenes

Basic Derivative	Produced Annually, 10^6 kg (last year reported)*	Uses, percent
Acrylonitrile	327	Apparel 70, home furnishings 30
Butadiene	909	SBR 40, polybutadiene 20, hexamethylenediamine 10
n-Butanol	341	Acrylates 30, glycol ethers 22, butyl acetate 12, solvent 11, plasticizers 9, amino resins 7
Butyl rubber	409	Tires, high-impact resins
Cumene	1864	Phenol and acetone 98
Dodecene (propylene tetramer)	120	Detergents, dodecyl sulfonate
Isopropyl alcohol	845	Acetone 43, process solvent 10, coating solvent 10, pharmaceutical and cosmetics 6
Nonene (propylene trimer)	162	Polyglycol ethers
Oxo alcohols (2-ethyl hexanol)	182	Plasticizers 65, acrylate esters 15
Polypropylene	1864	Injection molding 30, fibers and filaments 26, extrusion 11
Propylene oxide	818	Urethane polyols 54, propylene glycol 21, amines and ethers 13

*Usually 1981.

SOURCES: *Chem. Eng. News* and *Chem. Mark. Rep.*

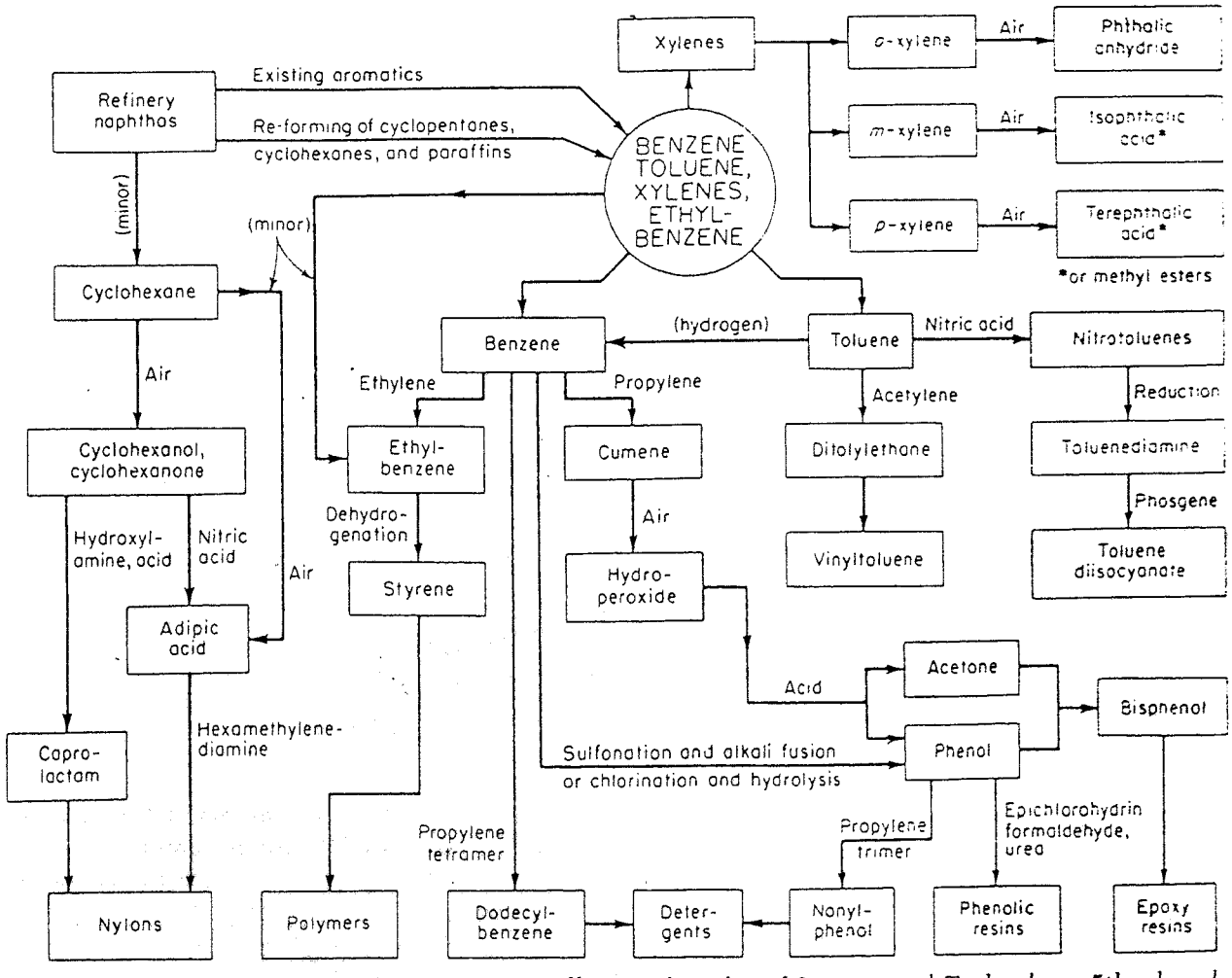

Fig. 38.4. Cyclic petrochemicals. *(McGraw-Hill Encyclopedia of Science and Technology, 5th ed., vol. 10, 1982, p. 67.)*

Table 38.6 Cyclic Petrochemicals

Basic Derivative	Produced Annually, 10^6 kg (last year reported)*	Uses, percent
Benzene	5285	Ethylbenzene 49, cumene 18, cyclohexane 15, nitrobenzene/aniline 5
Cyclohexane	682	Adipic acid 60, caprolactam 30
Ethylbenzene	3500	Styrene 99
Toluene	3339	Octane improver, benzene, xylene
Xylenes		
p-Xylene	1864	Dimethylterephthalate and terephthalic acid 100
o-Xylene	455	Phthalic anhydride
m-Xylene	n.a.†	Octane improver

*Usually 1981.

†n.a., not available

SOURCES: *Chem. Eng. News* and *Chem. Mark. Rep.*

in assured supply at very modest cost, in part due to chemical engineering advancement in effective separation processes. Research in conversion processes enabled low-valued molecules to be converted into more valuable ones. From these substances comes an almost unlimited supply of raw materials for expanding industry: antifreeze, lube oil additives, resins for plastics, synthetic fibers, and protective coatings.

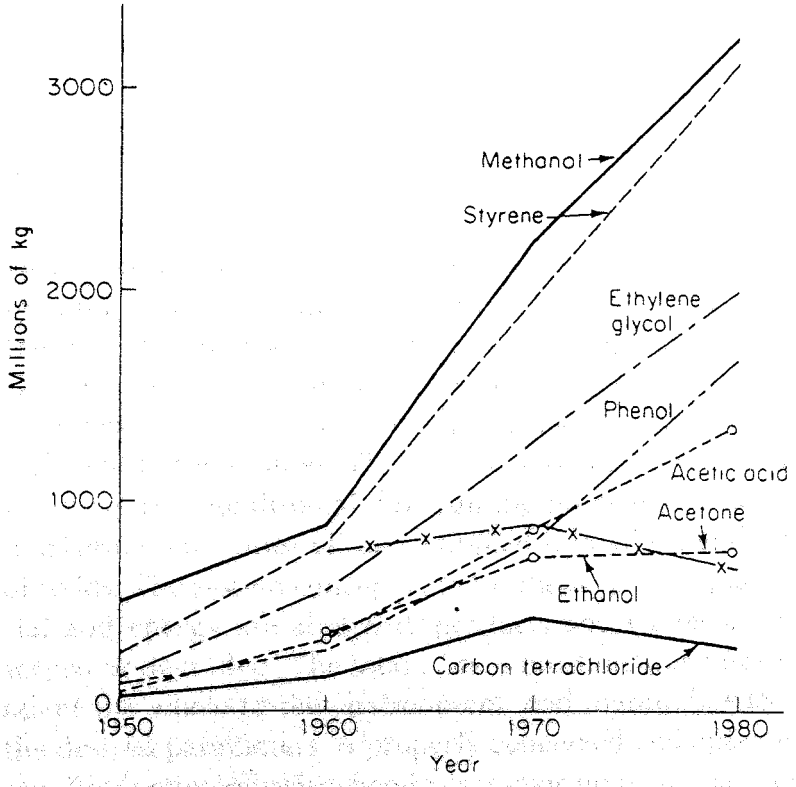

Fig. 38.5. Growth and production of important petrochemicals in the United States. *(United States International Trade Commission.)*

UNIT OPERATIONS (or Physical Separation Methods)

New understanding of the parameters affecting separative processes and the application of mathematics to such work enables better separations with lower energy consumption. The availability of adequate theory concerning such processes and the emergence of computer technology to make calculation and modeling less onerous has opened up whole new fields for work. The major unit operations that have been used are listed in Table 37.5 and are described in Chap. 37.

TRANSPORTATION. It is not generally recognized, but there are many miles of pipelines carrying such materials as ammonia and ethylene over considerable distances at low cost. The other low-cost transportation methods are ships, barges, and of course railways and trucks are used for smaller quantities.

CHEMICAL CONVERSIONS

Early years saw emphasis on a constantly increasing number of new products. As new product uses spread, many competed with one another for increasingly scarce feedstocks. More stress is now being laid upon new and cheaper methods of production than on new products. Many new reactions are more complicated and novel. Most new processes are continuous, and extensive use is made of instruments for analysis and control. Computer control has proved to be highly successful.

MANUFACTURE OF PETROCHEMICALS

Novel and efficient methods of manufacturing petrochemicals continue to be devised by the research and development departments of the various companies. It is convenient to examine these on the orderly basis of the chemical conversion types. Although rather old, the book by Groggins[3] is most useful in understanding these unit processes.

Discovering a suitable economical method to manage a known chemical reaction is not sufficient in these times. The control of quality, environmental effects of the product and by-products, sewage disposal, fire fighting procedures, start-up problems, safety, packaging and marketing, etc., must all be combined into a "system" utilizing professionals from a variety of fields. The system concept extends the scope of a plant beyond just processing where material and energy are absorbed, products and wastes are removed, and energy is either conserved or degraded. The total system must include information processing to sell and service, adapt the whole to the environment, and manipulate the summed information to maximize the desired parameters. A properly conceived and operated system offers no problems to society. Production of petrochemicals is enormous compared with other chemicals (over 2×10^9 kg/year for ethylene alone) as illustrated by the figures and tables, particularly Fig. 38.5.

[3]Groggins (ed.), *Unit Processes in Organic Syntheses*, 5th ed., McGraw-Hill, New York, 1958.

Probably the most notable new developments are the extensive use of selective catalysts to effect increased reaction rates and the improved recovery of heat that was formerly wasted because fuel was very cheap.

ALKYLATION, DEALKYLATION, AND HYDRODEALKYLATION.[4] The largest volume chemical alkylations are certainly benzene by ethylene to form ethylbenzene on the way to becoming styrene, discussed in Chap. 36; linear alkyl benzene for manufacturing detergents discussed in Chap. 26; and the benzene-propylene alkylation to form cumene from which phenol and acetone are derived. The alkylation of lead to form tetraethyl and tetramethyl lead is of diminishing importance as lead is phased out as a gasoline additive. The production of alkylated gasoline is larger than any of these, but the formed alkylates are not isolated and the products obtained are rarely considered to be chemical entities. Alkylation of gasoline is discussed in Chap. 37.

Cumene[5] is isopropyl benzene and is made by reacting benzene with propylene over a catalyst such as a phosphoric acid derivative at 250°C and 700 kPa. A refinery cut of mixed propylene-propane is frequently used instead of the more expensive pure propylene. Benzene is provided in substantial excess to avoid polyalkylation. Other catalysts which have been used are aluminum chloride and sulfuric acid.

Ethylbenzene[6] is made from benzene and ethylene using several modifications of the older mixed liquid-gas reaction system using aluminum chloride as a catalyst. One catalyst is proprietary, but not so corrosive as the usual Friedel-Craft catalysts. The reaction takes place in the gas phase over a fixed bed unit at 370°C under a pressure of 1450 to 2850 kPa. Unchanged and polyethylated materials are recirculated making a yield of 98 percent possible. The catalyst operates several days before requiring regeneration.

Dealkylation and hydrodealkylation are now practiced quite extensively to convert available molecules into others more desired. Two such processes practiced extensively are:

1. Toluene or xylene or C_9 and heavier aromatics + H_2 (presence of a dealkylation catalyst) = mainly benzene.
2. 2 toluene + a little H_2 (presence of a fixed bed catalyst) = benzene + mixed xylenes

Tetraethyl lead is prepared commercially by two processes. The first and older process involves the reaction between ethyl chloride and a sodium-lead alloy:

$$4PbNa + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

A newer electrolytic process[7] uses the Grignard reagent and an electrolytic cell to produce either TEL or TML:

$$2RMgCl + 2RCl + Pb \xrightarrow{\text{electric current}} PbR_4 + 2MgCl_2$$

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[4]Groggins, op. cit., p. 804; Sittig, *Aromatic Hydrocarbons*, Noyes, Park Ridge, N.J., 1976.

[5]Albright, Alkylation Processes, HF as a Catalyst, *Chem. Eng.* 73 (19) 205 (1966); Matox, *Trans. AIChE* 41 463 (1945).

[6]Dwyer, Lewis, and Schneider, Efficient, Non-polluting Ethylbenzene Process, *Chem. Eng.* 83 (1) 90 (1976).

[7]*Chem. Eng.* 72 (13) 102 (1965); 72 (23) 249 (1965); Electrolytic TEL, *Chem. Week* 94 (24) 77 (1964); Hard Hit Antiknocks Still Generate Cash, *Chem. Week* 132 (3) 50 (1983).

CRACKING OR PYROLYSIS. Cracking on a very large scale has been used for over 50 years to produce carbon black. This very useful substance is discussed in Chap. 8. Olefins and diolefins are made, mainly by catalytic cracking of various hydrocarbons, and the scale is very large. The most important product, produced at a rate of 12.7×10^9 kg/year is ethylene, with by-product propylene produced at a rate of 5.9×10^9 kg/year. It is made by steam cracking at 760 to 870°C with very short residence time. Quenching, followed by compression to 3.5 MPa, precedes separation processes. Ethylene, propylene, butadiene, and aromatics are all found in the product. Currently low-molecular-weight hydrocarbons (natural gas) are the preferred feedstocks, but increasing amounts will be made from heavy hydrocarbons.

Acetylene is made by cracking and is used in substantial quantities. Its manufacture is discussed in Chap. 7.

α-Olefins[8] for use in manufacturing detergents can be made by cracking heavy paraffins, but many α-olefins are made by oglimerization of lighter hydrocarbons, such as ethylene, and others by the Alfol process or the Ziegler process involving the use of trialkylaluminum. α-Olefins in the range of 12 to 18 carbon atoms are particularly desired for detergent alkylate because of their ready biodegradability.

DEHYDRATION. Dehydration is commonly used in the production of ethers by the dehydration of alcohols. Much diethyl ether is made by dehydrating ethyl alcohol with sulfuric acid as the dehydrating agent. Vapor phase dehydration over catalysts such as alumina is also practiced. Hydration of olefins to produce alcohols, usually over an acidic catalyst, produces substantial quantities of ethers as by-products. The reverse reaction, ethers to alcohols, can be accomplished by recycling the ethers over a catalyst.

ESTERIFICATION[9] WITH INORGANIC ACIDS. A variety of solvents, monomers, medicines, perfumes, and explosives are made from esters of nitric acid. Glycerol trinitrate, pentaerythritol tetranitrate (PETN), glycol dinitrate, and cellulose nitrate are discussed in Chap. 22.

ESTERIFICATION[10] OF ORGANIC ALCOHOLS AND ACIDS. Ethyl acetate has been an important solvent, particularly for lacquers, for many years. It is usually sold as an 85% solution and 10.6×10^9 kg was sold in the United States in 1980. Other esters made on a large scale are *n*-butyl acetate (53.7×10^6 kg/year) and isobutyl acetate (36.6×10^6 kg/year). Ester synthesis is relatively simple. The alcohol and an acid are heated together in the presence of a little sulfuric acid, and the reaction is driven to completion by removing the products as formed (usually by distillation) and employing an excess of one of the reagents. In the case of ethyl acetate, esterification takes place in a column which takes a ternary azeotrope (bp 70.2°C; 82.2% EtAc, 8.4% alcohol, 9% water) overhead. Alcohol can be added to the condensed overhead liquid to wash out the alcohol, which is then rectified and returned to the column to react.

Amyl, butyl, and isopropyl acetates are all made from acetic acid and the appropriate alcohols. All are useful lacquer solvents and their slow rate of evaporation (compared to acetone or ethyl acetate) prevents the surface of the drying lacquer from falling below the dew point, causing condensation on the film and a mottled surface appearance. This phenomenon

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[8]Freitas and Gum, Shell's Higher Olefins Process, *Chem. Eng. Prog.* **75** (1) 73 (1979).

[9]Groggins, op. cit., p. 694.

[10]Groggins, op. cit., p. 727; Lowenheim and Moran, *Industrial Chemistry*, 4th ed., Wiley-Interscience, New York, 1975, p. 350.

is known as "blushing." Other esters of importance are used in perfumery and in plasticizers. These include methyl salicylate, methyl anthranilate, diethyl-, dibutyl-, and di 2-ethylhexyl-phthalates.

Unsaturated vinyl esters for use in polymerization reactions are made by the esterification of olefins. The most important ones are vinyl esters: vinyl acetate (929×10^6 kg/year), vinyl chloride (2954×10^6 kg/year), acrylonitrile (327×10^6 kg/year), and vinyl fluoride. The addition reaction may be carried out in either the liquid, vapor, or mixed phases. The choice depends upon the properties of the acid. Care must be taken to reduce the polymerization of the vinyl ester produced.

Vinyl acetate[11] is manufactured by reacting ethylene with acetic acid in the vapor phase over a supported palladium catalyst.

$$H_2C{=}CH_2 + CH_3COOH + \tfrac{1}{2}O_2 \rightarrow CH_3COOCH{=}CH_2 + H_2O$$

The reaction is conducted in a fixed bed tubular reactor and is highly exothermic. With proper conditions, the only significant by-product is CO_2. Enough heat is recovered as steam to perform the recovery distillation. Reaction is at 175 to 200°C under a pressure of 475 to 1000 kPa. To prevent polymerization, an inhibitor such as diphenylamine or hydroquinone is added. Units for this process are quite large, some producing 50×10^6 kg/year.

An older process reacts acetylene with acetic acid in the liquid phase. Most vinyl acetate is now produced from ethylene.

Chloroprene, the monomer used in making neoprene, is a chlorovinyl ester of hydrochloric acid. It can be prepared by polymerizing acetylene to vinyl acetylene using a weak solution containing NH_4Cl, Cu_2Cl_2, and KCl as catalyst. The off-gas from the reactor has its water condensed out and is then fractionated. Aqueous hydrochloric acid at 35 to 45°C is then reacted with the vinyl acetylene in the presence of Cu_2Cl_2 to give chloroprene (2-chloro-1,3-butadiene):

$$2HC{\equiv}CH \xrightarrow{55\text{-}65^\circ C} \underbrace{CH_2{=}CH{-}C{\equiv}CH}_{\text{Vinyl acetylene}} + HCl \xrightarrow[40^\circ C]{Cu_2Cl_2} \underbrace{CH_2{=}\overset{\displaystyle Cl}{\overset{|}{C}}{-}CH{=}CH_2}_{\text{Chloroprene}}$$

Esters of allyl alcohol, e.g., diallyl phthalate, are used as bifunctional polymerization monomers. They can be prepared by simple esterification of phthalic anhydride with allyl alcohol. Several acrylic esters, such as ethyl or methyl acrylates, are also widely used and can be made from acrylic acid and the appropriate alcohol. The esters are more volatile than the corresponding acids.

HALOGENATION AND HYDROHALOGENATION.[12] Liquid and vapor halogenations have been studied and all produce mixes of products. The casual rule "you always get everything" seems to apply generally, and the greatest problem is often to direct the course of the reaction toward a preponderance of the desired product. It is frequently equally difficult to separate the multicomponent mix obtained.

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[11] *Hydrocarbon Process.* 60 (11) 234 (1981).

[12] Groggins, op. cit., p. 204; Belohlar and McBee, Halogenation, *Ind. Eng. Chem.*, annual review supplement, 1962, p. 77.

Most chlorinations produce HCl as a by-product, and for years a method was searched for to make this useful for chlorinations. The Deacon process was most frequently suggested. It employs the following reaction:

$$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$$

Because this is an equilibrium reaction not greatly favoring the right-hand side, and because most of the components are highly corrosive to common materials of construction, this reaction has never been really successful commercially. The reaction, however, can be used and driven to completion by use of the *oxychlorination* procedure. This reacts the chlorine with a reactive substance as soon as it is formed, thus driving the reaction to completion. Consider the oxychlorination of methane:

$$CH_4 + HCl + O_2 \rightarrow CH_3Cl,\ CH_2Cl_2,\ CHCl_3,\ CCl_4 + H_2O$$

+ some higher chlorinated hydrocarbons

This chlorination can be made with Cl_2, but a mole of HCl will be produced for every Cl introduced, and this must be disposed of to prevent environmental pollution. By-product HCl from other operations is frequently available at low cost. Cuprous and cupric chlorides, along with some potassium chloride as a molten salt catalyst, will speed up the reaction. Figure 38.6 shows a flowchart for a commercial installation. All waste chloro compounds are recirculated and consumed leaving only nonpolluting N_2, CO_2, and H_2O as effluents. The chloromethanes enjoy wide use and considerable production.

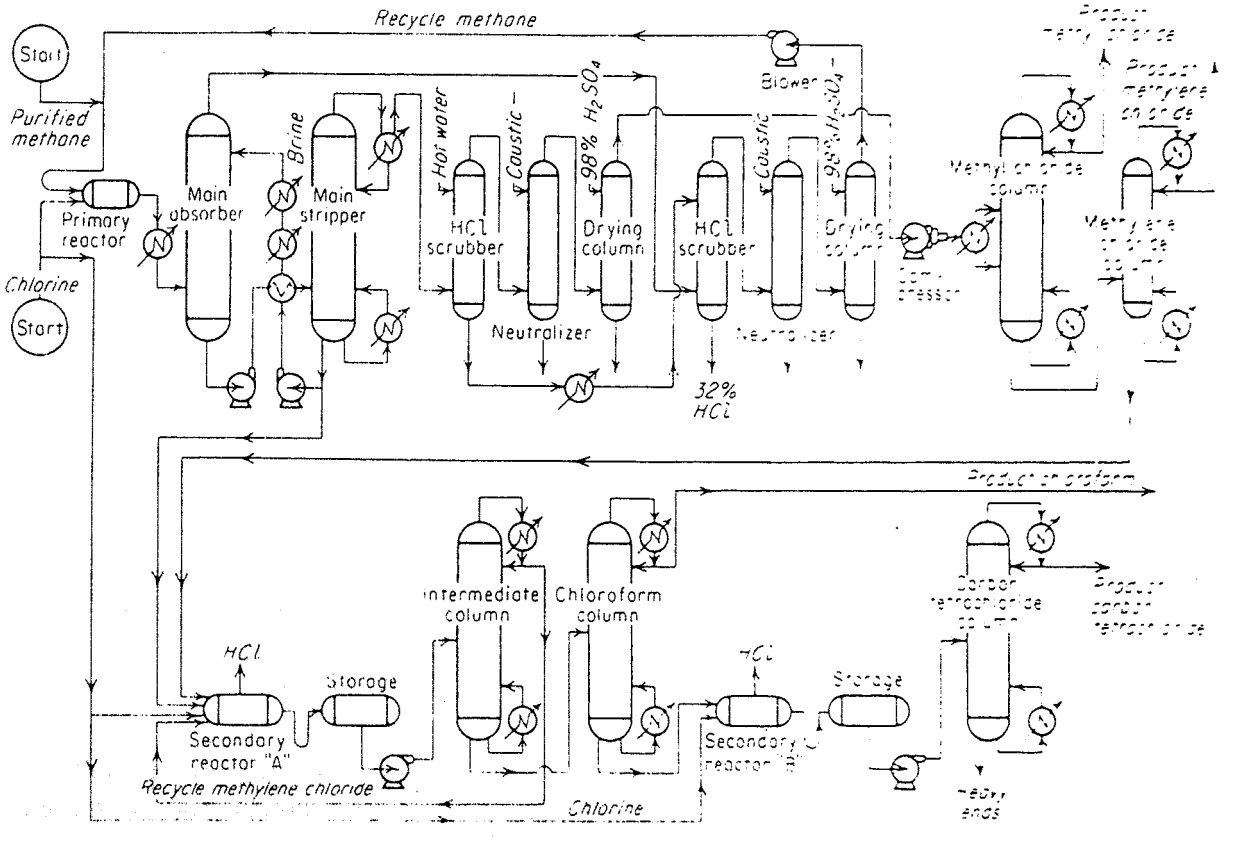

Fig. 38.6. Flowchart for chlorinating methane. The HCl scrubbers may be made of Karbate carbon. *(Petroleum Refiner.)*

Individual Chloromethane	Production in 10^6 kg/year (for 1980)	Uses, percent
Methyl chloride, CH_3Cl	177	Silicones 57, TML 9, methyl cellulose 4
Methylene chloride, CH_2Cl_2	254 227 (1982)	Paint remover 30, aerosol propellant 20, degreaser 10
Chloroform, $CHCl_3$	183	Fluorocarbons 90, miscellaneous
Carbon tetrachloride, CCl_4	322	Fluorocarbons 95, fumigant, degreasing

In Fig. 38.6, the chlorine and new and recycled methane are charged in the ratio 0.6/1.0. In the reactor, the temperature is maintained at 340 to 370°C. The chlorine conversion is total, and the methane conversion around 65 percent. Ignition is avoided by using narrow channels and high velocities in the reactor. The reaction product contains chlorinated hydrocarbons in the proportions: CH_3Cl, 6; CH_2Cl_2, 3; $CHCl_3$, 1; CCl_4, 0.25. There are also unreacted methane, HCl, Cl_2, and heavier chlorinated products. Secondary chlorinations take place at ambient temperature in a light-catalyzed reactor A which converts methylene chloride to chloroform, and in reactor B, which converts chloroform to carbon tetrachloride. By changing reagent ratios, temperatures, and recycling ratios, it is possible to vary the product mix somewhat to satisfy changing market demands.

Ethane Chlorination.[13] Ethane can be chlorinated under conditions very similar to those for methane to yield mixed chlorinated ethanes. Ethyl chloride (demand 214 × 10^6 kg in 1979) has been used mainly (90 percent) for making tetraethyl lead, and can be made by any one of three methods:

$$CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl \text{ (traditional chlorination)} \quad (1)$$

$$CH_2{=}CH_2 + HCl \xrightarrow{AlCl_3} CH_3CH_2Cl$$

(Friedel-Crafts olefin saturation to use up HCl from reaction 1) (2)

$$CH_3CH_3 + HCl + \tfrac{1}{2}O_2 \rightarrow CH_3CH_2Cl + H_2O \text{ (oxychlorination)} \quad (3)$$

Ethylene Dichloride.[14] When chlorine is added to olefins such as ethylene, many and mixed derivatives are formed; ethylene dichloride, dichloroethylene, trichloroethylene, tetrachloroethane, chloromethanes, and higher chloromethanes all form. Other halogens produce similar mixtures. With care, good yields of the desired product are possible. Ethylene dichloride, for example, can be prepared with 96 percent yield as follows:

$$H_2C{=}CH_2 + Cl_2 \rightarrow CH_2ClCH_2Cl$$

Ethylene bromide vapor (as catalyst) and Cl_2 gas meet a stream of ethylene in a chlorinating tower at 40 to 50°C. The tower has a partial condenser to strip out the ethylene bromide catalyst for recirculation, then a condenser-separator which separates unreacted ethylene for

[13]Shell Development, U.S. Patent 2,246,082; Lowenheim and Moran, op. cit., p. 371; Sittig, op. cit., p. 304; *Chem. Eng.* 81 (13) 114 (1974).

[14]Lowenheim and Moran, op. cit., p. 392.

recycle. Fractionation separates the higher-boiling materials. Oxychlorination can also be used to produce mixed products as in the case of methane. Ethylene dichloride is used in making ethylenediamine and Thiokol rubber.

Perchloroethylene (tetrachloroethylene, $CCl_2=CCl_2$)[15] is used for textile cleaning and vapor degreasing to the extent of 327×10^6 kg/year in 1981. 1,1,1-Trichloroethylene (283×10^6 kg/year in 1981) is usually made in the same apparatus or as a coproduct. Both chlorination and oxychlorination are used to supply the reagents needed. The reactions follow the same pattern as those for ethane and methane chlorination. Temperatures, pressures, and reagent ratios are somewhat different, however. *Trichloroethane* is used for vapor and cold degreasing, 62 percent; in adhesives, 12 percent; in aerosols, 10 percent; and in electronics, 6 percent.

Chlorinolysis is used to dispose of unwanted chlorinated hydrocarbons with one to three carbon atoms. These are reacted at high temperature (700°C) with chlorine to yield mixed carbon tetrachloride and perchloroethylene. These can be recycled to give other chlorinated products if desired. When trichloroethylene is made from acetylene, it can be carried through chlorination to pentachloroethane, then treated with milk of lime to form perchloroethylene, but this is rarely profitable.

HYDRATION AND HYDROLYSIS.[16] Synthetic ethyl alcohol (5.0×10^8 kg used in 1982) is generally thought of as the product of fermentation, but most is made by hydration of ethylene. Government interference in the market place and the demand for production from the huge surplus of grain have not changed the economics: alcohol from ethylene is purer and cheaper.

An older process dissolves ethylene in sulfuric acid to form ethyl sulfate, then hydrolyzes this to form ethanol. There is always some by-product ether which can be either sold or recirculated.

$$3H_2C=CH_2 + 2H_2SO_4 \rightarrow C_2H_5HSO_4 + (C_2H_5)_2SO_4$$
$$C_2H_5HSO_4 + (C_2H_5)_2SO_4 + H_2O \rightarrow 3C_2H_5OH + 2H_2SO_4 \text{ (dilute aq.)}$$

The yield is 90 percent with 5 to 10% as $C_2H_5OC_2H_5$. A direct hydration method Fig. 38.7

[15]*Hydrocarbon Process.* 60 (11) 195 (1981).

[16]Lowenheim and Moran, op. cit., p. 356; Groggins, op. cit., p. 750.

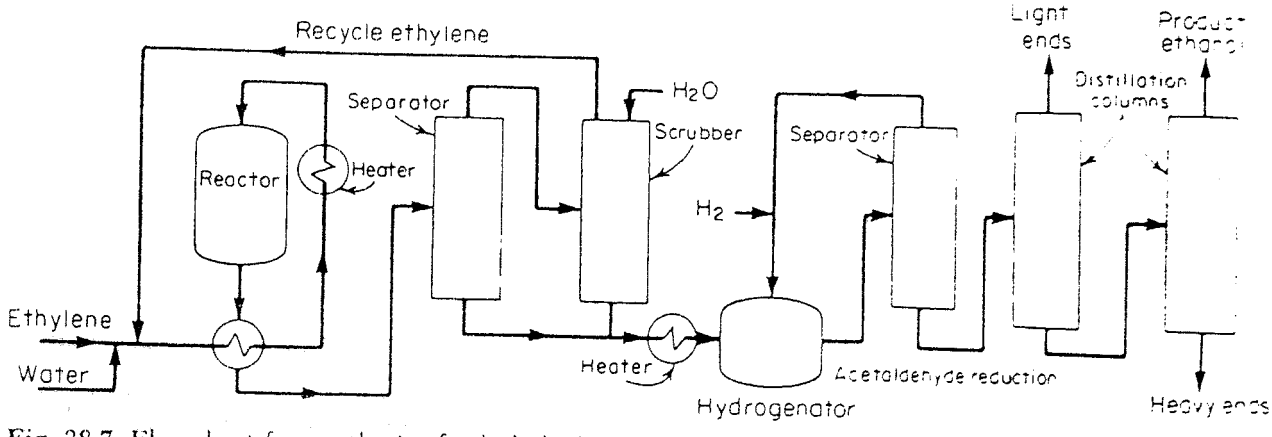

Fig. 38.7. Flowchart for synthesis of ethyl alcohol from ethylene by direct hydration.

is currently favored for over 85 percent of production:

$$CH_2{=}CH_2 + H_2O \xrightarrow[300°C\ 6.8\ MPa]{H_3PO_4} C_2H_5OH \qquad \Delta H = -40.2\ kJ$$

H_3PO_4 catalyst is used at 300°C and 6.8 MPa which gives a yield of 92 percent; conversion per pass is 4 to 25 percent, depending on the activity of the catalyst used. Ethylene and water are combined with a recycle stream in the ratio ethylene/water = 1/0.6 (mole ratio), a furnace heats the mixture to 300°C, and the gases react over the catalyst of phosphoric acid absorbed on diatomaceous earth. Unreacted reagents are separated and recirculated. By-product acetaldehyde is hydrogenated over a catalyst to form more alcohol.

Primarily because of political pressure and government subsidies, the production of fermentation alochol is growing astronomically. Much ethanol and methanol is finding its way into fuel mixtures, commonly known as gasohol. Brazil is conducting a major experiment in using pure alcohol as motor fuel. The results of these experiments remain economically unclear. Fermentation alcohol is discussed in Chap. 31 along with procedures for making absolute (anhydrous) alcohol. The maximum alcohol content obtainable by simple distillation is 95%, and this will not mix with gasoline. Anhydrous alcohol will mix with gasoline, but the addition of a small amount of moisture will cause it to separate out. It will absorb moisture from the air. Despite all these objections, it seems probable that alcohols will ultimately become fuels in substantial volume.

Isopropyl alcohol[17] is a widely used (8.4×10^8 kg in 1981) and easily made alcohol, the first petrochemical. It is used in making acetone, 23 percent (this use is falling because of competition from the cumene to phenol and acetone process—current use is probably considerably less than this); process solvent, 10 percent; cosmetics, 8 percent; and chemical derivatives, 6 percent. Four processes compete: (1) a sulfuric acid process similar to the one described for ethanol hydration, (2) a gas-phase hydration using a fixed-bed-supported phosphoric acid catalyst, (3) a mixed-phase reaction using a cation exchange resin catalyst, and (4) a liquid-phase hydration in the presence of a dissolved tungsten catalyst. Reactions 2, 3, and 4 are all essentially direct hydration procsses.

$$H_3C{-}CH{=}CH_2 + H_2O \xrightarrow{catalyst} CH_3CHOHCH_3$$

Per pass conversions vary from a low of 5 to a high of 70 percent for the gas-phase reaction. Reaction 1 is certainly obsolete because of the expense of using sulfuric acid and its pollution problems. The other processes are competitive, nonpolluting, and dependent on catalyst life and recycling problems for their economic life.

Secondary butanol can be made by processes similar to those described for ethylene and propylene.

HYDROGENATION, DEHYDROGENATION. Hydrogenation yields many useful chemicals, and its employment is increasing spectacularly, particularly in the petroleum refining industry. The cost of hydrogen is a major factor in restricting growth. For the production of hydrogen, see Chap. 7. Besides saturating double bonds, hydrogenation can be used to eliminate other elements from a molecule. These elements include oxygen, nitrogen, halogens, and particu-

[17]Onoue, Mizutani, Akiyama, and Izumi, Hydration with Water, *CHEMTECH* 8 (7) 432 (1978); *Hydrocarbon Process.* 60 (11) 182–184 (1981).

larly sulfur. Cracking in the presence of hydrogen is particularly effective in desulfuring heavy petroleum fractions, thus producing high-quality products. Although occasionally hydrogen for a reaction is provided by donor molecules and a few older reactions use hydrogen generated by acid or alkali acting upon a metal, gaseous hydrogen is the usual hydrogenation reagent. Hydrogenations are generally carried out in the presence of a catalyst and under elevated temperature and pressure. Noble metals, nickel, copper, and various metal oxide combinations are the common catalysts. Lower pressures and higher temperatures favor dehydrogenation, but the catalysts used are the same as for hydrogenation. Ammonia, not generally thought of as a petrochemical but certainly an important one, is discussed in Chap. 18.

Methanol[18] is manufactured by procedures very similar to those used for ammonia, using CO and H_2 from synthesis gas as raw materials and a copper-based catalyst (Fig. 38.8):

$$CO + H_2 \rightarrow CH_3OH \qquad \Delta H = -103 \text{ MJ}$$

Usage is large, 3.30×10^9 kg in 1982, and likely to become larger, perhaps huge. There is great interest in this material as an all-purpose fuel. Its production from biomass is being carefully studied, and the literature is full of speculative ideas.[19] Like ammonia, recent years have seen the usual synthesis pressure fall from 8 MPa to around 3 MPa. This has made the use of centrifugal compressors possible and resulted in considerable savings. New catalysts have helped push up the conversion. The older, high-pressure processes used zinc-chromium catalysts, but the low-pressure units use highly active copper catalysts; lately liquid-entrained micron-sized catalysts have been developed which can convert as much as 25 percent per pass. Contact of the synthesis gases with hot iron catalyzes competing reactions and also forms volatile iron carbonyl which fouls the copper catalyst. Some reactors are lined with copper. Table 38.7 shows the effect of temperature and pressure upon the methanol synthesis.

Synthesis gas is made and its composition adjusted as discussed in Chap. 6. Economical preparation of the gas is vitally important, for its cost constitutes nearly 75 percent of the final cost of the methanol. Both high- and low-pressure partial oxidation processes are used.

[18]Supp, Technology of Lurgi's Low Pressure Methanol Process, *CHEMTECH* 3 (7) 430 (1973).

[19]Frank, Methanol: Emerging Uses, New Syntheses, *CHEMTECH* 12 (6) 358 (1982); Haggin, Methanol: Future Fuel for Electric Utilities? *Chem. Eng. News* 60 (29) 41 (1982); McCallum et al., Alcohol Fuels for Highway Vehicles, *Chem. Eng. Prog.* 78 (7) 52 (1982).

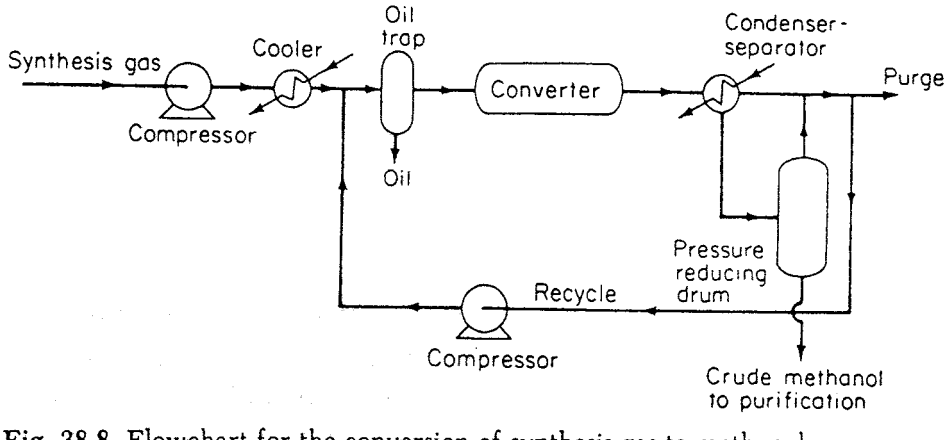

Fig. 38.8. Flowchart for the conversion of synthesis gas to methanol.

Table 38.7 Methanol Synthesis Data

Equilibrium Constants		Effect of Pressure on Equilibrium Conversion	
Temperature, °C	K_p	Pressure, MPa at 300°C	Percent Conversion to Liquid Methyl Alcohol in One Pass
200	1.7×10^{-2}	100	
300	1.3×10^{-4}	500	8.0
400	1.1×10^{-5}	1000	24.2
		2000	48.7
		3000	62.3

SOURCES: *Ind. Eng. Chem.* 32 147 (1940); Goldstean and Waddams, *Petroleum Chemicals Industry*, Spon, 1967, p. 55; cf. ammonia synthesis data and equipment in Chap. 18.

Because the catalyst is sensitive to sulfur, the gases are purified by one of several sulfur-removing processes, then are fed through heat exchangers into one of two types of reactors. With bed-in-place reactors, steam at around 4.5 MPa, in quantity sufficient to drive the gas compressors, can be generated. A tray-type reactor with gases introduced just above every bed for cooling offers more nearly isothermal operation but does not give convenient heat recovery. Figure 38.8 shows a flowchart for a Lurgi low-pressure plant. Pressure is 5 to 8 MPa, and the reactor temperature is 250 to 260°C. High- and low-boiling impurities are removed in two columns and the unreacted gas is recirculated. With changing market swings, some methanol plants have been converted into ammonia plants (and vice versa) without major change.

Styrene is produced from ethylbenzene by dehydrogenation; a flowchart is given in Fig. 36.3.

Many lower molecular weight aliphatic *ketones*[20] are made by dehydration of alcohols. Acetone, methyl ethyl ketone, and cyclohexanone can be made in this fashion. The production of cyclohexanone is considered later in this chapter under caprolactam.

Acetone is the ketone used in largest quantity (8.1×10^6 kg in 1981) and virtually all of it is now produced as a by-product of the manufacture of phenol via cumene. Manufacture from isopropanol is by the reaction:

$$(CH_3)_2CHOH\ (g) \xrightarrow[\text{acetate}]{\text{Cu or Zn}} (CH_3)_2CO\ (g) + H_2\ (g) \qquad \Delta H = -62.9\ \text{MJ}$$

This reaction takes place at around 200 kPa and 350°C giving 85 to 90 percent conversion. Purification by distillation follows. Because of competition and decreasing acetone demand, manufacture from isopropanol has fallen upon hard times and all U.S. plants are currently shut down. In periods of more normal business activity they make about one-third of the acetone used.

NITRATION.[21] Nitration offers a method of making unreactive paraffins into reactive substances without cracking. Because nitric acid and nitrogen oxides are strong oxidizing agents , oxidation always accompanies nitration. Aromatic nitrations have been important

[20]Ketones, *Hydrocarbon Process.* 60 (11) 174 (1981); Groggins, op. cit., p. 523.

[21]Groggins, op. cit., p. 60 ff.; Albright and Hanson (eds.), *Industrial and Laboratory Nitrations*, ACS, Columbus, Ohio, 1975.

since the turn of the century, particularly for the manufacture of explosives. Nitrobenzene (Chap. 39) is probably the most important nitration product. Certain esters of nitric acid (cellulose nitrate, PETN, glyceryl trinitrate) are often referred to as nitro compounds (nitrocellulose, nitroglycerin), but this terminology should be avoided.

Nitroparaffins.[22] Vapor-phase nitration of paraffin hydrocarbons, particularly propane, can be brought about by uncatalyzed contact between a large excess of hydrocarbon and nitric acid vapor at around 400°C, followed by quenching. A multiplicity of nitrated and oxidized products results from nitrating propane; nitromethane, nitroethane, nitropropanes, CO_2, etc., all appear, but yields of useful products are fair. Materials of construction must be very oxidation-resistant and are usually of ceramic-lined steel. The nitroparaffins have found limited use as fuels for race cars, submarines, and model airplanes. Their reduction products, the amines, and other hydroxy compounds resulting from aldol condensations have made a great many new aliphatic syntheses possible because of their ready reactivity.

AMINATION.[23] Amination, or reaction with ammonia, is used to form both aliphatic and aromatic amines. Reduction of nitro compounds is the traditional process for producing amines, but ammonia or substituted ammonias (amines) react directly to form amines. The production of aniline by amination now exceeds that produced by reduction (of nitrobenzene), Chap. 39.

Ethanolamines have been found to be very useful, for the alkalinity of the compounds varies with the degree of substitution, making a wide range of properties available from their salts. An equilibrium mixture of the three amines results when ethylene oxide is bubbled through 28% aqueous ammonia at 30 to 40°C. By recirculating the products of the reaction, altering the temperatures, pressures, and the ratio of ammonia to ethylene oxide, but always having an excess of ammonia, it is possible to make the desired amine predominate. Diluent gas also alters the product ratio.

$$H_2C{=}CH_2 \;(\text{O}) + NH_3 \text{ (excess)} \longrightarrow \begin{cases} HOCH_2CH_2NH_2 \text{ monoethanolamine} \\ (HOCH_2CH_2)_2NH \text{ diethanolamine} \\ (HOCH_2CH_2)_3N \text{ triethanolamine} \end{cases}$$

After the strongly exothermic reaction, the reaction products are recovered and separated by flashing off and recycling the ammonia, and then fractionating the amine products. Demand for the individual amines swings quite widely, so the process must be kept flexible to meet changing needs.

Methylamines are made by reacting gaseous methanol with a catalyst at 350 to 400°C and 2 MPa, then distilling the reaction mixture. Any ratio of mono-, di-, or tri-methylamines is possible by recirculating the unwanted products. In 1981, 102 × 10^6 kg of methylamines were consumed in the United States. Monomethylamine is used in explosives, 40 percent; insecticides, 33 percent; and surfactants, 8 percent. Dimethylamine is used for the manufacture of dimethylformamide and acetamide, 40 percent; pesticides, 14 percent; and water

[22]Bachmann and Pollack, *Ind. Eng. Chem.* 46 715 (1954); Albright, Nitration of Paraffins. *Chem. Eng.* 73 (12) 149 (1966).

[23]Ramioulle and David, Improved Methylamine Process, *Hydrocarbon Process.* 60 (7) 113 (1981).

treatment, 13 percent. Trimethylamine is used to form choline chloride, 70 percent, and to make biocides and slimicides, 20 percent.

Other alkylamines can be made in similar fashion from the alcohol and ammonia. Methyl, ethyl, isopropyl, cyclohexyl, and combination amines[24] have comparatively small markets and are usually made by reacting the correct alcohol with anhydrous ammonia in the vapor phase.

OXIDATION. Controlled oxidation is a valuable conversion method. The problem is to stop the reaction short of full combustion to CO, CO_2, and water. Usually it is desired to break C—H or C—C bonds and replace them with C—O bonds. The most readily available oxidant is air, but it contains a large quantity of unreactive nitrogen to carry away much heat and dilute the products, making their recovery more difficult. In a few rare cases, ozone is the preferred form of oxygen. Most oxygen has been separated from air, and the steel industry is the largest consumer, but the chemical industry consumes several thousand metric tons per day. Sittig points out that oxygen is often cheaper than air, largely because of increased yields, reduced recycle intervals, higher reaction rates, reduced equipment size, and reduced heat loss to nitrogen. Both liquid- and vapor-phase reactions are used industrially. All oxidation reactions are extremely exothermic, so heat removal can be a major problem. The commonest catalyst is V_2O_5, which becomes effective at about 400°C.

The Celanese Corporation has large plants at Bishop and Pampa, Tex., which oxidize propane and butane, separately or in LPG mixtures, to yield a variety of oxygen-containing chemicals. Better production has resulted from the use of oxygen, replacing air. Products produced include acetic acid, acetic anhydride, acetaldehyde, formaldehyde, acetone, butyraldehyde, ethyl acetate, butanol, and vinyl acetate. The cost of separating such mixtures forms an appreciable part of the cost of production. Catalyst selection for LPG oxidation gives some control over the product obtained. For example, liquid-phase oxidation of butane at 175°C and 5.5 MPa with a cobalt catalyst yields 60 percent acetic acid and 6 percent formic acid. Substitution of a manganese catalyst gives 62 percent acetic and 23 percent formic.

Phenol is currently made by two processes, both involving oxidation. The major process, through oxidation of cumene to cumene hydroperoxide, followed by decomposition to phenol and acetone is described in Chap. 34. A small amount of phenol is also made by the oxidation of toluene to benzoic acid, followed by decomposition to phenol.

Benzoic acid is synthesized to the extent of 382×10^6 kg/year. Most (54 percent) goes into phenol production, but significant amounts are used to make plasticizers, benzoyl chloride, sodium benzoate, and butyl benzoate. All U.S. producers use liquid-phase toluene oxidation over a cobalt naphthenate catalyst with air as the oxidizing agent. An older process[25] involving halogenation of toluene to benzotrichloride and its decomposition into benzoic acid is still used abroad.

Maleic acid and anhydride are recovered as by-products of the oxidation of xylenes and naphthalenes to form phthalic acids and are also made specifically by the partial oxidation of benzene over a V_2O_5 catalyst. This is a highly exothermic reaction, and several modifications of the basic process exist[26] including one using butylenes as the starting materials.

Partial oxidation is also used to raise the temperature and thus bring about the decompo-

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[24]Combination Amines, *Hydrocarbon Process.* 60 (11) 146 (1981).

[25]Lowenheim and Moran, op. cit., p. 138.

[26]Wohlfahrt and Emig, Compare Maleic Anhydride Routes, *Hydrocarbon Process.* 59 (6) 83 (1980).

sition of hydrocarbons. Examples are the manufacture of carbon black (Chap. 8) and acetylene (Chap. 7).

In Europe, *formic acid* is made by the oxidation of formamide. "All formic acid produced in the United States is produced as a by-product of the liquid phase oxidation of *n*-butane to acetic acid."[27] The by-product source is expected to dry up in the future, and the most promising route to replace it is through carbonylation of methanol.

Caprolactam, adipic acid, and hexamethylene diamine[28] are all made from cyclohexane. Almost all high-purity cyclohexane is obtained by hydrogenating benzene, although some for solvent use is obtained by careful distillation of selected petroleum fractions.

Several oxidative routes are available to change cyclohexane to cyclohexanone, cyclohexanol, and ultimately to adipic acid or caprolactam. If phenol is hydrogenated, cyclohexanone can be obtained directly; this will react with hydroxylamine to give cyclohexanone oxime which converts to caprolactam on acid rearrangement (Chap. 35). Cyclohexane can also be converted to adipic acid, then adiponitrile, which can be converted to hexamethylenediamine. Adipic acid and hexamethylenediamine are used to form nylon 6,6. This route to HMDA is competitive with alternative routes through butene.

Acetaldehyde has a brisk sale as a precursor of acetic acid, 1,3-butylene glycol, glyoxal, pentaerythritol, peracetic acid, and pyridines. The demand in 1981 was 409 × 10^6 kg. There are several competing processes. (1) The older process by the hydration of acetylene is no longer significant. (2) The Wacker process developed by Hoechst[29] starts with ethylene and oxidizes it directly with air or 99% oxygen (Fig. 38.9). The catalyst is palladium chloride with a copper chloride promoter. The ethylene gas is bubbled, at atmospheric pressure, through the solution at its boiling point. The heat of reaction is removed by boiling of the water. Unreacted gas is recycled following condensation of the aldehyde and water, which are then separated by distillation. (3) Passing ethyl alcohol over a copper or silver gauze catalyst gives

[27]Aquilo and Horlenko, Formic Acid, *Hydrocarbon Process.* 59 (11) 120 (1980).

[28]Lowenheim and Moran, op. cit., p. 201.

[29]Acetaldehyde, *Hydrocarbon Process.* 60 (11) 121 (1981).

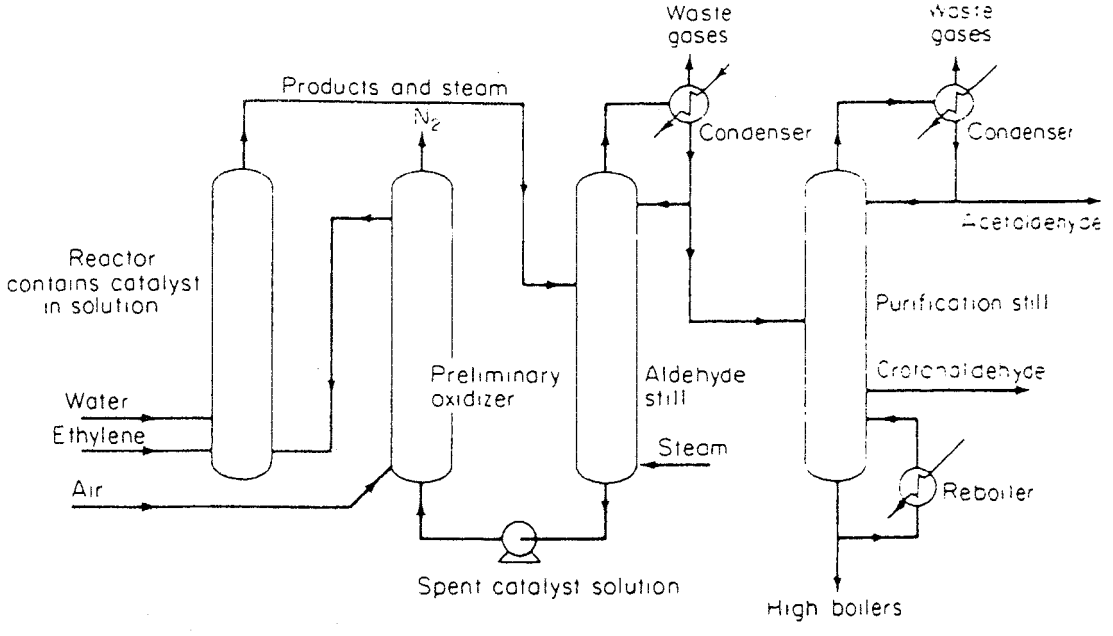

Fig. 38.9. Flowchart for acetaldehyde by air oxidation of ethylene.

about a 25 percent conversion to acetaldehyde, with recirculation making a 90 to 95 percent yield possible. (4) Lower molecular weight paraffin hydrocarbons are oxidized noncatalytically to produce mixed compounds, among them acetaldehyde and acetic acid. Separation of such mixtures is difficult.

Since nearly 50 percent of the acetaldehyde produced is used to make acetic acid, its future market is questionable. Acetic acid produced directly by the carbonylation of methanol[30] has already cut deeply into the market.

Acetic acid is widely used, and much is converted to acetic anhydride.[31]

Eastman[32] is currently building a very large plant to produce these and other chemicals from coal. The reaction between ketene and acetic acid produces the anhydride, but the amount of energy required to produce the ketene (acetone is cracked to give ketene and methane) is very large.

$$(CH_3)_2CO \rightarrow CH_2{=}C{=}O + CH_4$$
$$CH_2{=}C{=}O + CH_3COOH \rightarrow (CH_3CO)_2O$$

Ketene is used immediately after manufacture because it does not store well. The major use of acetic anhydride is in making vinyl acetate and other acetylations.

Ethylene glycol,[33] used in antifreeze, 40 percent, and in fibers and films, 50 percent, is a major petrochemical and has been for many years. The demand in 1981 was 2×10^9 kg. Like most of the other alcohols, it was originally made by reacting chlorine and water (HOCl) with ethylene to form the chlorohydrin, which was then hydrolyzed to yield glycol. This procedure and several others (formaldehyde + CO_2, fermentation, oxidation of propane) is now technically and environmentally obsolete. The currently favored process starts with ethylene and reacts it with oxygen or air in a tubular reactor over a silver oxide catalyst to form ethylene oxide. Because the volatility of glycol is low, it is preferable to purify the ethylene oxide, then convert it to glycol by hydration. During the hydration, however, polyglycols, particularly di- and tri-ethyleneglycols are formed. The reactions are:

$$H_2C{=}CH_2 + 1/2\ O_2 \xrightarrow{Ag_2O} CH_2{-}CH_2 \text{ (epoxide O)} + (CO_2 \text{ and } H_2O \text{ by combustion})$$

$$CH_2{-}CH_2 \text{ (epoxide O)} + H_2O \longrightarrow HO{-}CH_2{-}CH_2{-}OH + \text{polyglycols}$$

Ethylene dichloride (under 1 ppm) is added to a mix of ethylene and air in the ratio of 1:10 to reduce oxidation to CO_2, and the mixture is passed over a supported silver oxide catalyst at atmospheric pressure and 280°C with a 1-s contact time. This causes a 60 to 70 percent

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[30]Roth et al., Low Pressure Process for Acetic Acid via Carbonylation of Methanol, *CHEMTECH* 1 (10) 600 (1971).

[31]Jeffreys, *The Manufacture of Acetic Anydride*, 2d ed., The Institution of Chemical Engineers, London, 1964.

[32]A Giant Step: Acetic Anhydride from Coal, *Chem. Week* 127 (3) 40 (1980).

[33]*Hydrocarbon Process.* 60 (11) 161–163 (1981).

conversion of the ethylene. Ethylene oxide is removed from the effluent by water scrubbing, and the unreacted constituents are recirculated.

Liquid-phase conversion of the ethylene oxide to glycol uses a dilute sulfuric acid solution at 60°C and is a quite slow reaction, requiring 30 min to 1 h. An excess of water is used, and the mono-, di- and triethylene glycols are separated by vacuum distillation.

Aromatic products by oxidation include the phthalic acids from xylenes or naphthalene (see Fig. 38.4 and Table 38.6), vanillin from eugenol (Chap. 27), toluene to benzaldehyde and benzoic acid, cumene to cumene hydroperoxide, and benzene to maleic acid and anhydride. These have all been discussed elsewhere in this book.

HYDROFORMYLATION, THE OXO-REACTION. The oxo-reactions offer ways of converting α-olefins to aldehydes and/or alcohols containing an additional carbon atom. For example (Fig. 38.10):

$$CH_3CH{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO$$
$$CH_3CH_2CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2CH_2OH$$

The olefin in a liquid state is reacted at 27 to 30 MPa and 150 to 170°C in the presence of a soluble cobalt catalyst. The aldehyde and a lesser amount of the alcohol are formed, flashed off along with steam, and the catalyst is recycled. Conversions of over 97 percent are obtained. The reaction is strongly exothermic. The CO and H_2 are usually in the form of synthesis gas. When propylene is used as the hydrocarbon, *n*- and iso-butyraldehyde are formed. This reaction is most frequently run with the C_3 and C_7 to C_{12} olefins. When C_7 olefins are used, a series of dimethyl- and ethylhexanols and methyl heptanols are formed which are used as "octyl" alcohols to make plasticizers and esters.

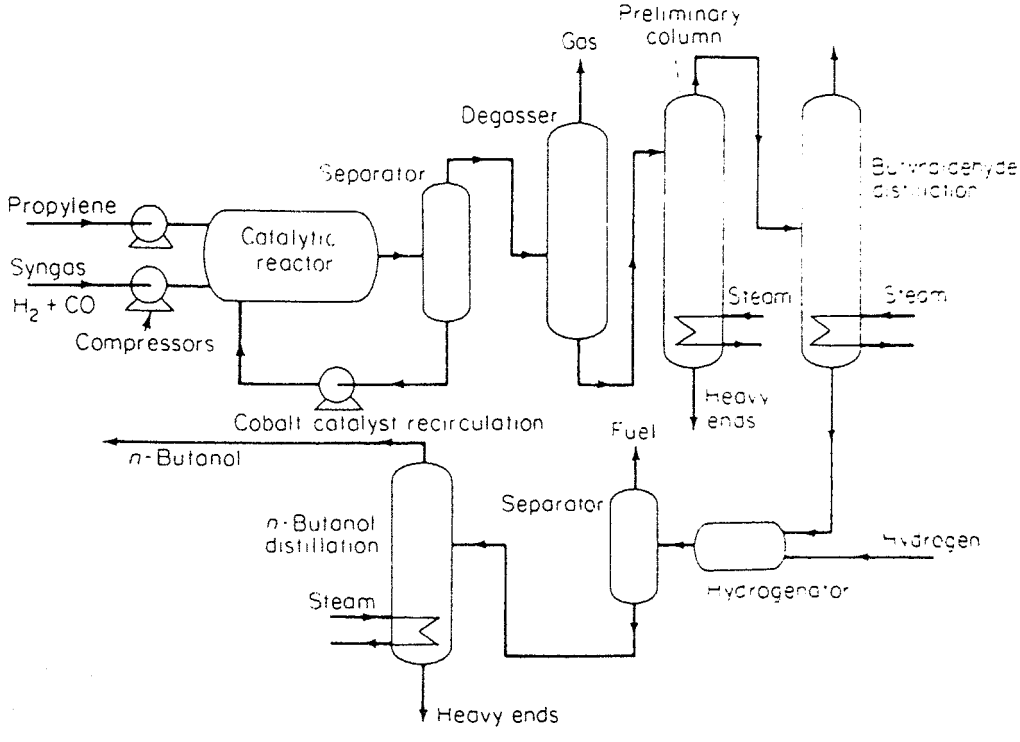

Fig. 38.10. Flowchart for butraldehyde and *n*-butanol by the oxo-synthesis

POLYMERIZATION. Polymerization has been covered already for a variety of processes. In Chap. 37, polymerization of low-molecular-weight hydrocarbons to form gasolines was examined. The reactions considered in Chaps. 34, 35, and 36 are mainly polymerizations.

MISCELLANEOUS. *Methyl tertiary butyl ether, MTBE,*[34] has excited considerable interest in recent years because it is a good octane enhancer for gasoline (it blends as if it had a research octane number of 115 to 135). It also offers a method of selectively removing isobutylene from a mixed C_4 stream, thus enabling the recovery of high-purity butene-1. Interest also arises because the MTBE can be isolated, then cracked to yield highly pure isobutylene and methanol. One plant uses this procedure to make pure tertiary butyl phenol (5×10^7 kg in 1981), and another is considering its use to make polyisobutylenes. The reaction for making MTBE proceeds quickly and highly selectively by reacting a mixed butene-butane fraction with CH_3OH in the liquid phase on a fixed bed of ion-exchange resin catalyst (Fig. 38.11). The reactions are:

$$CH_3OH + (CH_3)_2C{=}CH_2 \rightarrow CH_3OC(CH_3)_3$$

Reactor effluent is distilled, giving MTBE of 99% purity. A few percent of isobutylene remain unchanged and can be scavenged by use of a second unit.

Constantly increasing quantities of sulfur are recovered from refining operations and the processing of natural gas. Hydrodesulfurization frees sulfur, usually as H_2S, from the heavier fractions of petroleum, and this can be recovered. Frasch sulfur is more expensive than recovered sulfur, so it has become the material which supplies deficits of sulfur after the recovered sulfur is used up. This is precisely the condition in which acetone from isopropyl alcohol manufacturers find themselves. Sulfur is recovered by variants in the Claus process.

Carbon disulfide[35] is used principally for the manufacture of rayon. The traditional route[36] was by an electrothermal process using coal and sulfur, but most is now made by a catalyzed

[34]Stinson, New Plants, Processes Set for Octane Booster, *Chem. Eng. News* **124** (26) 35 (1979); Taniguchi and Johnson, MTBE for Octane Improvement, *CHEMTECH* 9 (8) 502 (1979); *Hydrocarbon Process.* **61** (9) 177 (1982).

[35]Haines, Carbon Disulfide, *Ind. Eng. Chem.* 55 (6) 44 (1963).

[36]See CPI 2, p. 336.

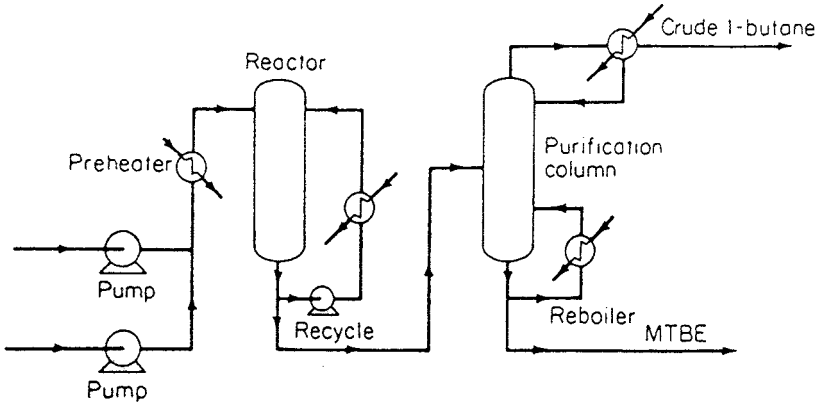

Fig. 38.11. Flowchart for methyl tertiary butyl ether (MTBE) and 1-butene manufacture.

reaction between methane and sulfur. The reactions are:

$$C + 2S \rightarrow CS_2$$

$$CH_4\,(g) + 4S\,(g) \xrightarrow[700°C\ 270\ kPa]{Al_2O_3 \text{ or } Cr_2O_3} CS_2\,(g) + 2H_2S\,(g) \qquad \Delta H = +81.6\ MJ$$

The yield, based on methane, is around 90 percent per pass. The H_2S can be converted to sulfur and reused, or reacted with carbon to form more CS_2. Demand in 1980 was 171×10^6 kg.

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Chapter 6

Cyclic Intermediates and Dyes

HISTORICAL. Chemistry's first big breakthrough into the public eye came with the proliferation of quality dyestuffs replacing expensive, chronically short, and generally low-quality natural dyes. In those days, aromatic chemicals, usually in quite impure form, came exclusively from coal tar and neither their structure nor reactions were well understood. Sir William Henry Perkin discovered the first practical synthetic dye (mauve) while trying to synthesize quinine from aniline contaminated with toluidine. Since all dyes came from compounds derived from coal tar and most required the use of aniline, the synthetic dyes became known as coal-tar or aniline dyes. Sir Henry realized the importance of his discovery, patented it, and dominated the synthetic dye industry for seventeen years (1856 to 1873). He became quite rich in the process and retired at an early age to a life of scientific experimentation. Particularly after his retirement, the Germans and Swiss rapidly became leaders in the field and by 1914 the Germans made 87 percent of the world's dyes. World War I cut off the supply of German dyes, and this led the United States to establish a domestic industry. The dye industry has always been highly competitive, and the United States has recently lost a significant percentage of its domestic market to Swiss, German, Japanese, and Italian competition. There are several major American companies that have dropped dye manufacture since 1978.

ECONOMICS AND USES. Dyes generally have rather complicated structures which are made by reactions involving building blocks known as intermediates. Most of these are aromatic compounds with substituent groups such as $-NH_2$, $-OH$, $-NO_2$, and $-SO_3H$ which alter the reactivity of the cyclic compound and sometimes the color of the dye. Intermediates are not used just for the manufacture of dyes, but for all types of organic work where complex structures are built up. They are particularly useful for making agricultural chemicals, pesticides, pharmaceuticals, and rubber chemicals. Table 39.1 shows the size of the markets involved. This specialized business produces around 2000 compounds, most at rates of 0.5 to 1.5×10^6 kg/year. Most intermediates sell for around $1.00 per kilogram. These substituted aryl compounds are usually made from benzene, toluene, or naphthalene, and their price goes up as the number and complexity of the substituents increase. Many are made by batch processes, and good chemistry is required to assure preparation of the isomer desired. Where a 1,4-substitution is desired, the 1,2- and 1,3-substituted material may be of value only as a fuel. Making these unwanted materials, however, comsumes valuable raw material to form potential (often actual) polluters.

There is an astonishingly large literature concerning reactions of aromatic compounds, much of it going back to the nineteenth century. Some of the information is still highly useful and valuable today.

Table 39.1 Synthetic Organic Chemicals and Their Raw Materials: U.S. Production and Sales

	Production, 10^6 kg		Sales			
			Quality, 10^6 kg		Value, 10^6 $	
	1972	1980	1972	1980	1972	1980
Tar	3,396	1,970	1,549	1,422	40	n.a.*
Tar crudes	3,608	n.a.	2,411	n.a.	126	n.a.
Crude products from petroleum and natural gas	39,451	54,651	21,773	29,224	1,177	10,645
Synthetic Organic Chemicals						
Cyclic intermediates	15,894	20,486	7,362	9,118	1,434	7,248
Dyes	120	111	116	103	480	791
Synthetic organic pigments	30	32	24	28	149	361
Medicinal chemicals	106	111	74	76	490	1,153
Flavor and perfume materials	50	80	47	59	88	254
Plastic and resin materials	11,782	17,357	10,430	15,250	4,258	16,011
Rubber processing materials	164	132	127	88	178	296
Elastomers	2,234	2,168	1,880	1,481	1,095	2,280
Plasticizers	1,836	811	1,026	715	451	858
Surface-active agents	n.a.	2,206	n.a.	1,354	n.a.	1,296
Pesticides and other agricultural products	526	667	465	639	1,092	4,078
Miscellaneous chemicals	41,125	53,623	20,525	22,825	4,680	15,171
Grand total	120,322	154,405	67,809	82,382	15,738	n.a.

*n.a., not available

The whole procedure of intermediate manufacture is generally labor intensive, which makes it difficult for United States companies to compete. The recent emphasis on identification and control of toxicants has provided additional harassment. Determining the toxicity of materials that are made in such small quantities may well cost more than years of potential profit.

RAW MATERIALS. Both inorganic and organic materials are needed to make dyes and intermediates, but the backbone of the raw-material sequence is:

Petroleum→aromatic hydrocarbons→intermediates→dyes

Aromatic hydrocarbons were once scarce, at least in the high purities desired for making cyclic intermediates, because of the scarcity of coal tar and the difficulty in separating it into pure materials. The abundance of raw materials now available from petroleum is not an unmixed blessing, for there is fierce competition for many fractions which are desired by other users. At the same time, there remain interesting aromatic fractions of coal tar for which uses have never been developed and which are simply burned.

The demands of the dye industry for raw materials from which to make intermediates, or precursors of intermediates, played a major part in bringing about the change from beehive to by-product coke ovens. The source of the major hydrocarbons desired for making intermediates, e.g., benzene, toluene, naphthalene, anthracene, xylene, and some paraffins and

olefins, is now the special aromatized naphthas resulting from the catalytic refining of selected petroleum crudes. Under 1 percent are coal-derived.

For some complicated intermediates, the use of inorganic acids, bases, and halogens in manufacture is surprisingly high. There are anthraquinone dyes that require over 75 kg of chemicals to produce 1 kg of dye.

INTERMEDIATES

A few intermediates are made in very large quantities and enjoy their principal use outside the field of dyes. Many, originally extracted from coal tar, are now made synthetically. See Table 39.2. The following intermediates were made in quantities in excess of 400×10^6 kg in 1980 (note that most of these have already been covered in other chapters): ethyl benzene, dimethylterephthalate, *p*-xylene, cumene, and phenol. Isocyanates, *o*-xylene, alkyl benzenes, phthalic anhydride, cyclohexanone, aniline, nitrobenzene, bisphenol A, monochlorobenzene, and toluene-2,4-diamine were produced on a lesser, but still very large scale. These two sets account for nearly 90 percent of the total output of intermediates, but this chapter is concerned primarily with the other 10 percent.

The census of intermediates taken by the U.S. International Trade Commission shows that in 1980 the United States produced 2.05×10^{10} kg of cyclic intermediates, a 9 percent decline from the previous year, caused primarily by the general decline in business. These materials were valued at $7.27 million.

Table 39.2 Production of Important Cyclic Intermediates (in thousands of kilograms

	1972	1980
Acetanilide, technical	1,474	4,357
Aniline	186,282	299,737
Benzoic acid, technical	70,684	33,370
Chlorobenzene, mono	183,411	128,560
Cresols, total	48,306	47,927
Cresylic acid, refined, total	24,991	17,395
Cumene	1,042,273	1,572,273
Cyclohexane	1,044,545	892,727
Cyclohexanone	356,109	348,552
o-Dichlorobenzene	28,357	22,175
p-Dichlorobenzene	35,144	34,115
Ethylbenzene	2,580,000	3,473,640
4,4′-Isopropylidenediphenol (bisphenol A)	115,995	240,767
α-Methylstyrene	16,999	17,612
Nitrobenzene	250,531	278,012
5-Nitro-*o*-toluenesulfonic acid	3,644	
Nonylphenol	45,589	66,927
o-Xylene	378,083	452,239
p-Xylene	1,003,636	1,926,363
Phenol	952,784	1,167,045
Phthalic anhydride	433,172	371,930
Salicylic acid, technical, sales	21,407	17,750
Styrene	2,700,454	3,116,360

Unit Operations

No operations are used in intermediates manufacture that have not been described in previous chapters, particularly Chap. 38.

Chemical Conversions

The chemical conversions of this chapter are mainly concerned with aryl substances; those of Chap. 38 with aliphatic and naphthenic substances, but the conversions involved and the general approaches to manufacture are strikingly similar. In manufacturing petrochemicals, the focus was not so much on the effect of the substitution on subsequent reactions as it is for cyclic intermediates, but the reactions are similar.

ISOMERS. With benzene, monosubstitution produces a single substance, but with naphthalene and anthraquinone, there are two possible monosubstitutions. With polysubstitution, the possibilities for isomers become quite large. The ability to react to form the substance desired, or to yield the color or physiological reaction wanted, depends on creating the correct isomer, largely to the exclusion of all others. Here chemical skill is of the utmost importance, for some substituents encourage ortho and para substitution, others encourage meta. Rules for substitution, the early ones based upon observation and surmise and later ones based on physical chemical theory, are covered in detail in several works on intermediate synthesis.[1] Substituents are important beyond their contribution to molecular geometry in that they can alter the solubility of the molecule in acid or basic solvents and possess directional effects on ensuing nucleophilic substitutions.

NITRATION. Before the ability to work with and control high pressures became commonplace, thus enabling ammonolysis to be run readily, the standard way to put an amino group on an aryl nucleus was by nitration, then reducing the aryl nitro compound to an amine. The amino-substituted compound could then be subjected to the diazotation reaction by treating it with $NaNO_2$ in cold solution. This reactive material could then be coupled with another compound to give the azo configuration, the major chemical group for many dyes. Very few nitro groups appear in finished dyes. Most have been reduced to the more reactive amine in the course of dye formation.

A typical nitration reaction is:

$$ArH + HNO_3 \text{ (conc. } H_2SO_4) \rightarrow ArNO_2 + H_2O \text{ (more dilute } H_2SO_4) \qquad \Delta H = -60 \text{ to } -150 \text{ kJ}$$

The presence of sulfuric acid in quantity is vital to the success of the nitration because: (1) it reduces the ionization $HNO_3 \rightleftharpoons H^+ + NO_3^-$ which increases as the water-producing reaction dilutes the reaction mixture. Additional strongly oxidizing NO_3^- ions cause destruction of the organic reactants and products. (2) It acts as an energy reservoir to prevent destructive rapid temperature rise and provides a vehicle to convey heat to the jacket and/or coil. (3) It

[1]ECT, 3d ed., vol. 8, 1979, p. 159 ff; Rys and Zollinger, *Fundamentals of the Chemistry and Application of Dyes*, Wiley-Interscience, New York, 1972; Fierz-David and Blangey, *Fundamental Processes of Dye Chemistry*, Interscience, New York, 1949.

increases the solubility of the hydrocarbon in the reaction mix, thus speeding up the reaction. (4) It promotes the ionization of the nitric acid to give NO_2^+, the nitronium ion, which is the nitrating species. The nitronium ion is formed as follows.

In Mixed Nitric-Sulfuric Acid (Commonly Called Mixed Acid)

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

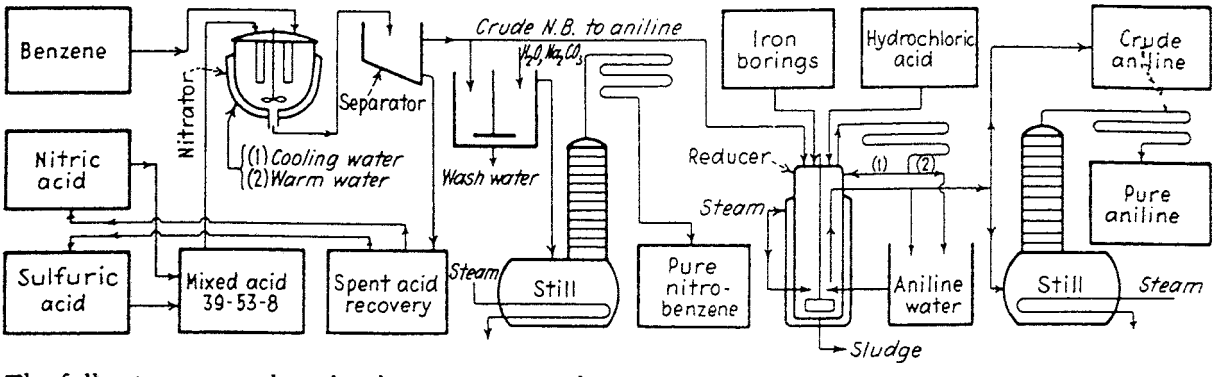
In Nitric Acid

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

Absorption of water by sulfuric acid favors the nitration reaction and shifts the equilibrium to the right. Considerable heat evolution accompanies the nitration reaction, oxidation increases it, and the heat of dilution of the sulfuric acid increases it still farther. Increased temperature favors dinitration and oxidation so the reaction must be cooled to keep it under control. Good heat transfer can be assured by the use of jackets, coils, and good agitation in the nitrator. Nitrators are usually made of stainless steel, although cast iron stands up well against mixed acid. Figure 39.1 gives some data for nitrobenzene manufacture. Lists of important nitrations along with notes concerning the raw materials used and some details of manufacture are available.[2]

Most commercial nitrations are made with mixed acid, but there are other useful nitrating

[2]CPI 4, p. 717; Abrahart, *Dyes and Their Intermediates*, Pergamon, Oxford, 1977; Groggins, *Unit Processes in Organic Syntheses*, McGraw-Hill, New York, 1958.



The following materials and utilities are required to produce:

NITROBENZENE, 1 t			
Benzene	655 kg	Sodium carbonate	10 kg
HNO_3	530 kg	Power (% of total cost)	3.2
H_2SO_4	721 kg	Labor (% of total cost)	2.4
H_2O	109 kg	Overhead (% of total cost)	8.3

ANILINE, 1 t			
Nitrobenzene	1390 kg	Power (% of total cost)	6.4
Iron borings	1600 kg	Labor (% of total cost)	8.0
HCl (30%)*	125 kg	Overhead (% of total cost)	4.0

**Or an equivalent amount of aniline salt mother liquor.*

Fig. 39.1. Flowchart for production of nitrobenzene and aniline by reduction.

agents, e.g., inorganic nitrates, oxides of nitrogen, nitric acid + acetic anhydride, and nitric + phosphoric acid.

Example of a Technical Nitration. Nitrobenzene from benzene is used mainly for reduction to aniline, where it must compete with aniline by ammonolysis.

$$C_6H_6 + HNO_3\,(H_2SO_4) \rightarrow C_6H_5NO_2 + H_2O\,(H_2SO_4) \qquad \Delta H = -113\ \text{kJ}$$

Plants are simple with large (3000 to 5000 L) nitrators operating batchwise or small continuous (Biazzi or similar) units. The temperature is held at about 50°C, governed by the rate of feed of benzene. Reaction is quite rapid (15 to 20 min) in well-stirred and continuous nitrators. The reaction products are decanted from the spent acid and are washed with dilute alkali. The spent acid is sent to some type of recovery system. Yields of 98 percent of theory are common.

SULFONATION. Since sulfuric acid is comparatively cheap, it is desirable to use it for nucleophilic substitution wherever possible. The fundamental chemistry has been well studied[3] and a list of important sulfonations is available.[4]

The reaction may be expressed as:

$$ArH + (HO)_2SO_2 \rightarrow ArSO_2OH + H_2O$$

The usual sulfonating agent is concentrated sulfuric acid, but SO_3, chlorosulfonic acid, metallic sulfates, and sulfamic acid are also occasionally used. For each substance being sulfonated, there is a critical concentration of acid below which sulfonation ceases. The removal of the water formed in the reaction is therefore essential. The use of a very large excess of acid, while expensive, can maintain an essentially constant concentration as the reaction progresses. It is not easy to volatilize water from concentrated solutions of sulfuric acid, but azeotropic distillation can sometimes help. Sulfonations are exothermic, but not highly corrosive, so they can be conducted in steel, stainless-steel, or cast-iron sulfonators. A jacket heated with hot oil, Dowtherm, or steam can serve to heat the contents sufficiently to get the reaction started, then carry away the heat of reaction. A good agitator, a condenser, and a fume control system are usually also provided.

Example of a Technical Sulfonation. 1- and 2-Naphthalene sulfonic acids are formed simultaneously when naphthalene is sulfonated with concentrated sulfuric acid. The isomers must be separated if pure α- or β-naphthol are to be prepared from them, and this offers some difficulty. Variations in time, temperature, sulfuric acid concentration, and acid/hydrocarbon ratio alter the yields to favor one particular isomer, but a pure single substance is never formed. Using similar acid/hydrocarbon ratios, sulfonation at 40°C yields 96% alpha isomer, 4% beta, while at 160°C the proportions are 15% alpha, 85% beta.

The α-sulfonic acid can be hydrolyzed to naphthalene[5] by passing steam at 160°C into the

[3]Venkataraman, *The Chemistry of Synthetic Dyes*, several volumes, Academic, New York, 1952–1974; Groggins, op. cit., p. 303.

[4]CPI 3, p. 723.

[5]Shreve, beta-Naphthol, *Color Trade J.* **14**, 42 (1924); Groggins, op. cit., p. 316.

sulfonation mass. The naphthalene so formed passes out with the steam and can be recovered. The pure beta acid left behind can be hydrolyzed by caustic fusion to yield relatively pure β-naphthol.

Isolation of a specific isomer is rarely this simple. Separations are based on some of the following consideration:

1. Variations in the *rate* of hydrolysis of two isomers (as above).
2. Variations in the solubility of various salts in water.
3. Differences in solubility in solvents other than water.
4. Differences in solubility accentuated by common-ion effect (salt additions).
5. Differences in properties of derivatives.
6. Differences based on molecular size, such as using molecular sieves or absorption.

The fourth edition of CPI[6] gives an extensive list of commercial sulfonations.

AMINATION BY REDUCTION. Color in dyes frequently results from conjugated systems involving nitrogen and these are formed from amino groups. For years, the only method of putting an amino group on an aryl nucleus involved adding an $-NO_2$ group, then reducing. Without high-pressure vessels and modern catalysts, reduction had to be done by reagents which would function under atmospheric pressure. The common reducing agents available under these restrictions are: (1) iron and acid, (2) zinc and alkali, (3) sodium sulfide or polysulfide, (4) sodium hydrosulfite, (5) electrolytic hydrogen, and (6) metal hydrides. Now liquid and gas phase hydrogenations can be performed on a variety of materials. The typical reaction is:

$$RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$$

The energy given off by this type of reaction is quite large.

Where metals are used to produce the reducing hydrogen, several difficult processing problems are created. The expense is so great that it is necessary to find some use for the reacted material. Spent iron can sometimes be used for pigment preparations or to absorb H_2S. Stirring a vessel containing much metal is quite difficult.

On a small scale, hydrogen for reduction can be produced by cracking ammonia. Transport and storage of hydrogen as ammonia is compact, and the cracking procedure involves only a hot pipe packed with catalyst and immersed in a molten salt bath. The nitrogen that accompanies the generated hydrogen is inert.

Example of a Technical Amination by Reduction. Aniline Production. In 1982, 3.09 $\times 10^8$ kg of aniline were produced, 55 percent of which were used to make *p,p'*-methylene diisocyanate, 20 percent went into rubber chemicals, and only 10 percent into intermediates and dyes. Most was made by catalytic reduction of nitrobenzene with hydrogen, which is practiced as shown in Figs. 39.2 and 39.3.

AMINATION BY AMMONOLYSIS. The replacement of a nuclear substituent such as $-OH$, $-Cl$, or $-SO_3H$ with $-NH_2$ by the use of ammonia has been practiced for some time with molecules having labilizing substituents (groups nearby making replacement easier). For example, 1,4-dichloro-2-nitrobenzene can be changed readily to 4-chloro-2-nitroaniline by

[6]CPI 4, p. 724.

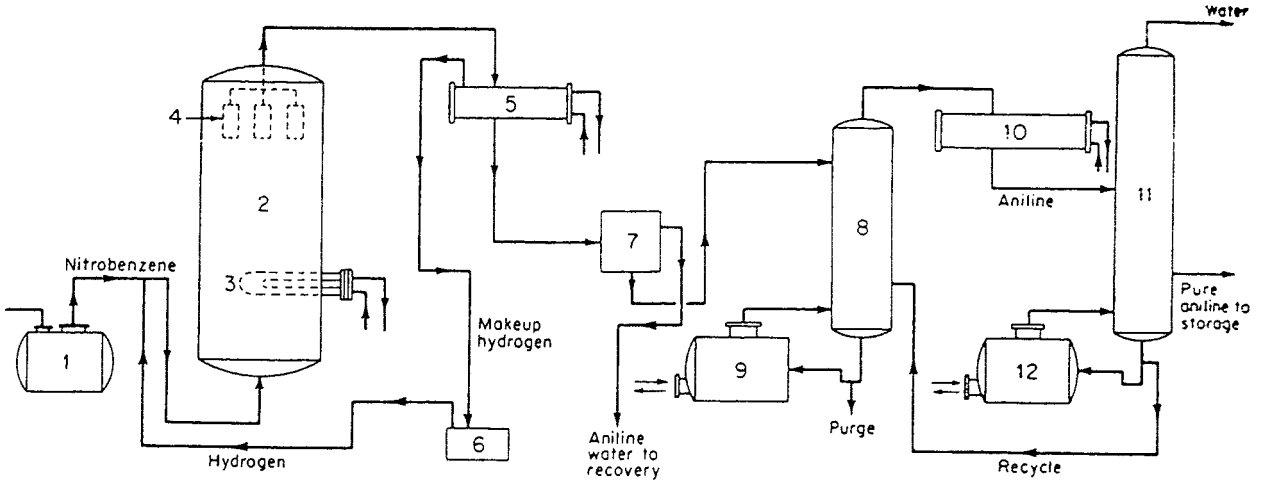


Fig. 39.2. Continuous fluid-bed vapor-phase reduction of nitrobenzene. (1) Nitrobenzene vaporizer, (2) reactor with fluidized catalyst bed, (3) cooling tubes, (4) catalyst filters, (5) product condenser, (6) hydrogen recycle compressor, (7) aniline water settler and decanter, (8) crude aniline still, (9) reboiler for crude aniline still, (10) condenser, (11) aniline finishing still, (12) reboiler for aniline finishing still. *(American Cyanamid Co.)*

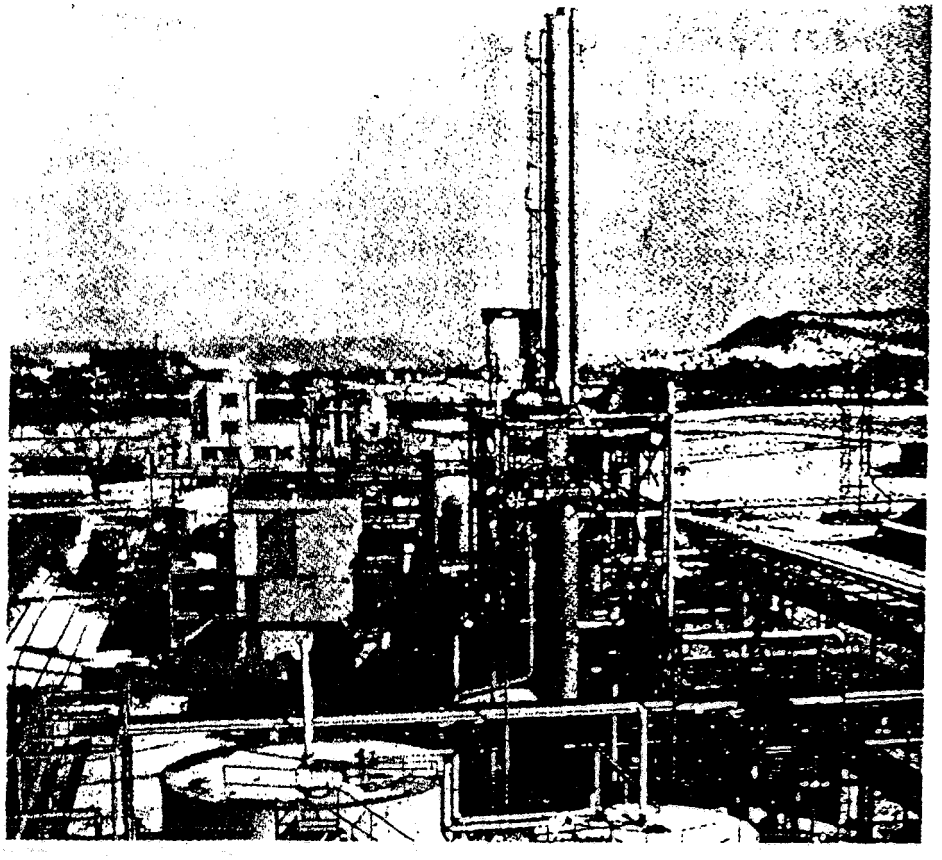


Fig. 39.3. Overall view of the vapor-phase aniline manufacturing facilities at Willow Island, W. Va. *(American Cyanamid Co.)*

treatment with aqueous ammonia. Other molecules offer more processing difficulty, and pressure vessels are required for the production of aniline[7] from chlorobenzene or phenol

$$C_6H_5OH + NH_3 \rightarrow C_6H_5NH_2 + H_2O$$

Ammonia is a comparatively low-cost reagent. The other routes to amines through reduction use expensive reagents (Fe, Zn, or H_2 gas) that make ammonolysis costs quite attractive. Substituted amines can be produced by using substituted ammonia (amines) in place of simple ammonia.

Equipment is some type of agitated pressure vessel made entirely of iron; stainless steel is rarely necessary. Figure 39.4 shows a flowchart for the manufacture of aniline from phenol.[7] Lists of intermediates made by ammonolysis and the conditions involved are available.[8]

HALOGENATION.[9] Halogenation is almost always chlorination, for the difference in cost between chlorine and the other halogens, particularly on a molal basis, is quite substantial. In a very few cases, Br, I, or F confer properties special enough to warrant the additional expense, but large-scale operations are not based on them. Chlorine and hydrochloric acid are used to cause substitution (and occasionally addition) on aryl ring compounds. Chlorination proceeds (1) by addition to an unsaturated bond, (2) by substitution for hydrogen, or (3)

[7]McKechnie, Bayer, and Drennan, Aniline: Phenol Feed Chosen, *Chem. Eng.* 87 (26) 26 (1980). Polinski and Harvey, Aniline Production by Dual Function Catalyst, *Ind. Eng. Chem., Prod. Res. Develop.* 10 (4) 365 (1971).

[8]Groggins, op. cit., chap. 8; CPI 4, p. 721.

[9]Groggins, op. cit., chap. 6.

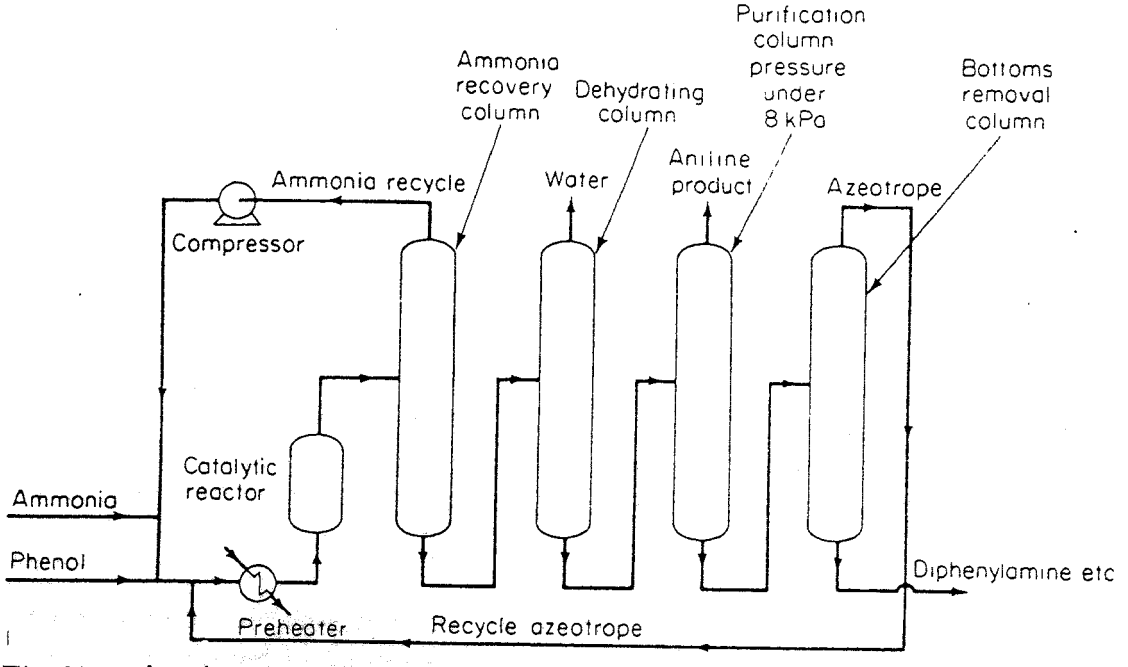
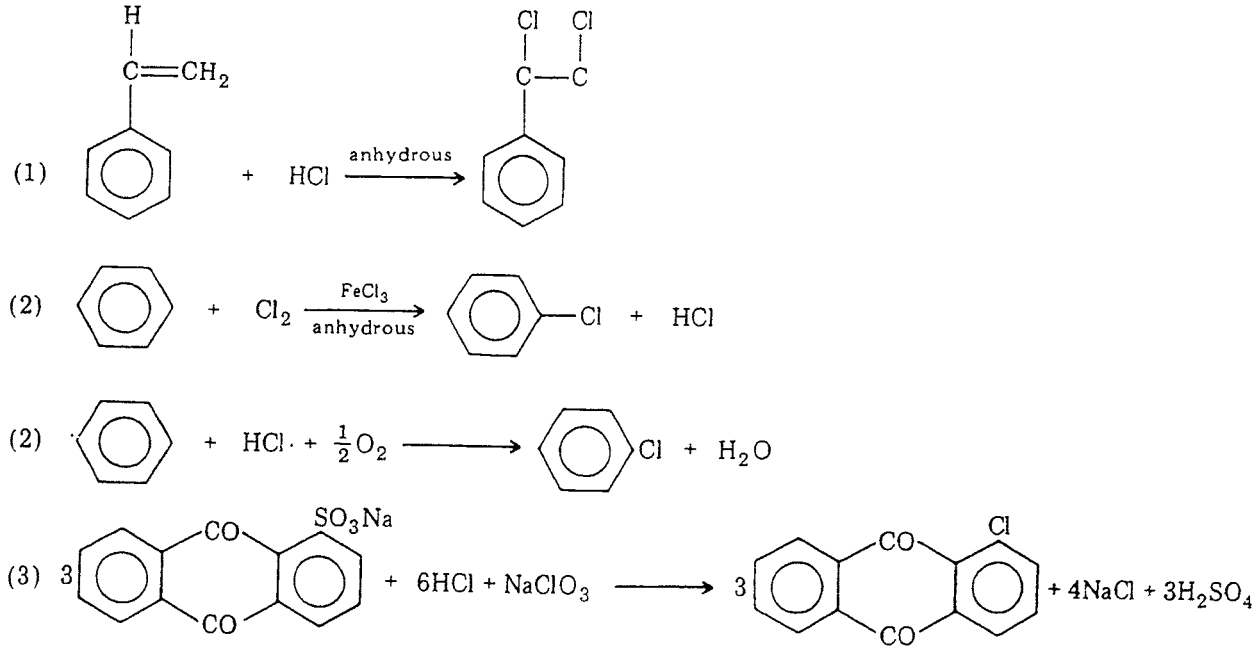


Fig. 39.4. Flowchart for aniline from phenol.

by replacement of another group such as $-OH$ or $-SO_3H$. Examples are:



Reaction (3) can be run in hot, dilute, aqueous solution. Chlorinations are considerably less orderly than nitrations and sulfonations. Substitution rules are not as reliable since isomer distribution is influenced by hydrocarbon/chlorine ratios, and there is usually a considerable range of isomers formed. Light catalyzes some chlorinations, temperature has a profound effect, and polychlorination almost always occurs to some degree. All halogenations are strongly exothermic.

Equipment for chlorinations is more difficult to select than for most other unit processes. The combination of halogen, oxygen, halogen acid, water, and heat is particularly destructive to metals. A few alloys, such as Hastelloy and Durichlor, resist well, but they are expensive and difficult to machine. Glass, glass-enameled steel, and tantalum are totally resistant but not always affordable. Anhydrous conditions permit operation with steel or nickel alloys.

Technical Example of Chlorination. Chlorobenzene. Chlorobenzene enjoys a modest use as a solvent and for the manufacture of nitrochlorobenzenes. Its former uses for manufacturing phenol and aniline are gone. It is manufactured by passing dry chlorine through benzene using ferric chloride as a catalyst:

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$$

The reaction rates favor production of monochlorobenzene over dichlorobenzene by 8.5:1 providing that the temperature is maintained below 60°C. The HCl generated is washed free of chlorine with benzene, then absorbed in water. Distillation separates the monochlorobenzene, leaving mixed isomers of dichlorobenzene to be disposed of.

HYDROLYSIS. Replacement of $-SO_3H$ or $-Cl$ with $-OH$ is frequently desired and is usually accomplished by fusion with alkali. Polysubstituted molecules may be hydrolyzed with

less drastic conditions. Besides alkaline substances, hydrolysis is brought about by enzymes, acids, or sometimes water alone.

A typical reaction is:

$$ArSO_3Na \text{ (or ArCl)} + 2NaOH \rightarrow ArONa + Na_2SO_3 \text{ (or NaCl)} + H_2O$$

Acidification will give ArOH. SO_2 or CO_2 may be sufficiently acidic to "spring" the ArOH. Most hydrolysis reactions are modestly exothermic.

Cast iron or steel open fusion pots heated to the high temperatures required (200 to 325°C) with oil, electricity, Dowtherm, or quite commonly directly with gas, are standard equipment.

Examples of Technical Hydrolyses. Phenol was at one time made by the fusion of benzene sulfonic acid with caustic soda, but the present method via cumene is cheaper. The hydrolysis of chlorobenzene to phenol requires far more drastic conditions and is no longer competitive. Ethylene chlorohydrin can be hydrolyzed to glycol with aqueous sodium carbonate. Hydrolysis uses a far wider range of reagents and operating conditions than most of the previously discussed chemical conversion processes. Even at the present cost of electricity, a 750 J/s (1 HP) motor can be used for about four hours for the cost of 1 kg of NaOH, so great interest prevails in manufacturing for the substitution of energy for chemicals.

The following chemicals, many previously discussed, have hydrolysis involved in their manufacture:

Cellulose → glucose
Pentosans → furfural
Ethyl hydrogen sulfate → ethyl alcohol
Starch → glucose
Propane → glycerol
Fats → fatty acids + glycol
Aryl and alkyl halides → alcohol
Olefins → alcohols

ALKYLATION OF AMINES. Alkylation is usually used to increase the resistance of dyes to shade changes when exposed to dilute alkalis or acids. For example, dihydroxybenzanthrone is alkylkated with dimethyl sulfate to produce vat green 1. The usual alkylating agents for amines are varied but include alcohols, alkyl halides, dialkyl sulfates, and the methyl ester of *p*-toluenesulfonic acid. Jacketed autoclaves with stirrers and internal cooling coils are used, for some reactants are volatile and require pressure for containment.

Technical Example of Alkylation. Dimethylaniline. Dimethylaniline is employed in the manufacture of a number of triarylmethane dyes. It is prepared according to the reaction:

$$C_6H_5NH_2 + 2CH_3OH \xrightarrow{H_2SO_4} C_6H_5N(CH_3)_2 + 2H_2O$$

Aniline, with a considerable excess of methanol and a little sulfuric acid, is heated in an autoclave at about 200°C for 5 or 6 h. The pressure rises to around 3.7 MPa. Vacuum distillation is used for purification.

OXIDATION.[10] Control is the major problem where oxidation is practiced. Only partial oxidation is wanted as one organic compound is converted into another. It is simple enough to

[10]Groggins, op. cit., chap. 9; Sittig, *Combining Oxygen and Hydrocarbons for Profit*, Gulf, Houston, Tex., 1962.

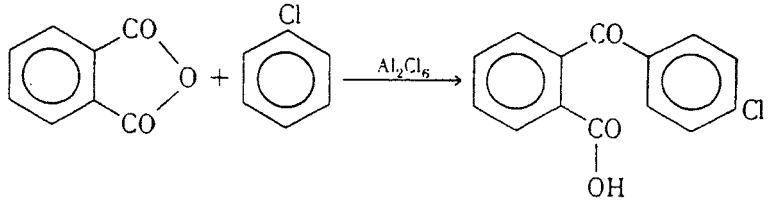
make CO_2 and H_2O from organic substances, but once started, it is difficult to stop oxidation before it is completed. The commonest reagent is air, but oxygen frequently proves to be less expensive. The chemical oxidizing agents, nitric acid, dichromates, permanganates, chromic anhydride, chlorates, and hydrogen peroxide, are usually an order of magnitude more expensive than the gases, so they are employed only when the gases do not function well. The combustion reaction is extremely exothermic:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad \Delta H = -2.41 \text{ MJ}$$
$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -2.85 \text{ MJ}$$

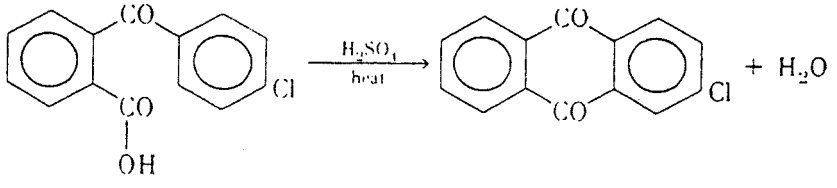
Since some complete combustion always accompanies partial oxidation, heat removal is frequently the controlling factor in oxidations.

Technical Example of Oxidation. Phthalic acids and anhydride, produced primarily from xylenes, are used in the manufacture of several dyes, plastics, and plasticizers. Their production is covered in Chap. 34. The anhydride is converted to anthraquinone, to phthalocyanines, and phenolphthalein, along with several other derivatives. Phenol (Chap. 34) is also made from cumene by oxidation. These two substances have become so widely used that the part going into dyes has become almost trivial.

CONDENSATION AND ADDITION REACTIONS (FRIEDEL-CRAFTS). There are only a few products manufactured in any considerable tonnage by these reactions, but those which are find use in several different intermediates and particularly in making high-quality vat dyes. The agent employed in this reaction is usually an acid chloride or anhydride, catalyzed with aluminum chloride. Phthalic anhydride reacts with chlorobenzene to give *p*-chlorobenzoylbenzoic acid:



in a continuing action, the *p*-chlorobenzoylbenzoic acid forms β-chloroanthraquinone by ring closure.



Since anthraquinone is a relatively rare and expensive component of coal tar and petroleum, this type of reaction has been the basis for making relatively inexpensive anthraquinone derivatives for use in making many fast dyes for cotton. A list[11] of important intermediates made using addition reactions is available.

Friedel-Craft reactions are highly corrosive, and the aluminum-containing residues are difficult to dispose of.

[11]CPI 4, p. 727.

MISCELLANEOUS CONVERSIONS. Every reaction ever disclosed by an organic chemist is available and potentially valuable for the production of some intermediate. Among these are acylation, carboxylation, and ring closure. A list[12] of compounds made commercially by these less common processes is available.

DYES

Dyes add value to products far beyond their cost. Frequently the color of a product is the reason for its sale. Some dyes have special uses, such as radiation detectors and photosensitive dyes for papers and posters. The purpose of a dye is usually to help the purchaser sell his product to his customer. Dye sales in 1980 were estimated at $608 million. Every dye sale is estimated to influence $10 in product sales, so the effect is far greater than the cost. Typical dye molecules appear complicated and confusing, but their synthesis follows an orderly procedure, using about 1000 intermediates and comparatively few chemical conversions.

A dye must be colored, but it must also be able to impart color to something else on a reasonably permanent basis before it can be considered as a dye. Most dyes contain considerable unsaturation, and some part of the dye is usually in the form of aromatic rings with nitrogen unsaturation of several types common to many dyes. The quinoid structure appears frequently. The dye tree of Fig. 39.5 shows the development of several major dyes and their discovery dates. Obviously, the dye industry boomed when chemistry was in its infancy.

Many correlations have been made (and more attempted) between chemical structure and color. Color results from electronic transitions between molecular orbitals. Some early observations are still worth studying and are easier to comprehend than electronic structures. These concepts began to be used as early as 1876 and reached their present state about 1930.

A dye consists of a color-producing structure, the *chromogen* (electron acceptor), and a part to regulate the solubility and dyeing properties, the *auxochrome* (electron donor). Without both parts, the material is simply a colored body.

The chromogen is an aromatic body containing a color-giving group, commonly called the *chromophore*. Chromophore groups cause color by altering absorption bands in the visible spectrum. Common chromophores are:

1. The nitroso group: $-NO$ (or $=N-OH$)
2. The nitro group: $-NO_2$ (or $=NOOH$)
3. The azo group: $-N=N-$
4. The ethylene group: $\geq C=C \leq$
5. The carbonyl group: $\geq C=O$
6. The carbon-nitrogen groups: $\geq C=NH$ and $-CH=N-$
7. The carbon-sulfur groups: $\geq C=S$ and $\geqq C-S-S-C \leqq$

These groups add color to aromatic bodies by causing displacement of, or an appearance of, absorbent bands in the visible spectrum. The chromophore groups are the basis of one method of dye classification.

Some molecules lose their colors when the chromophore groups are saturated. The auxochromes, the part of the dye which causes it to adhere to the material which it colors (usually

[12]CPI 4, p. 728.

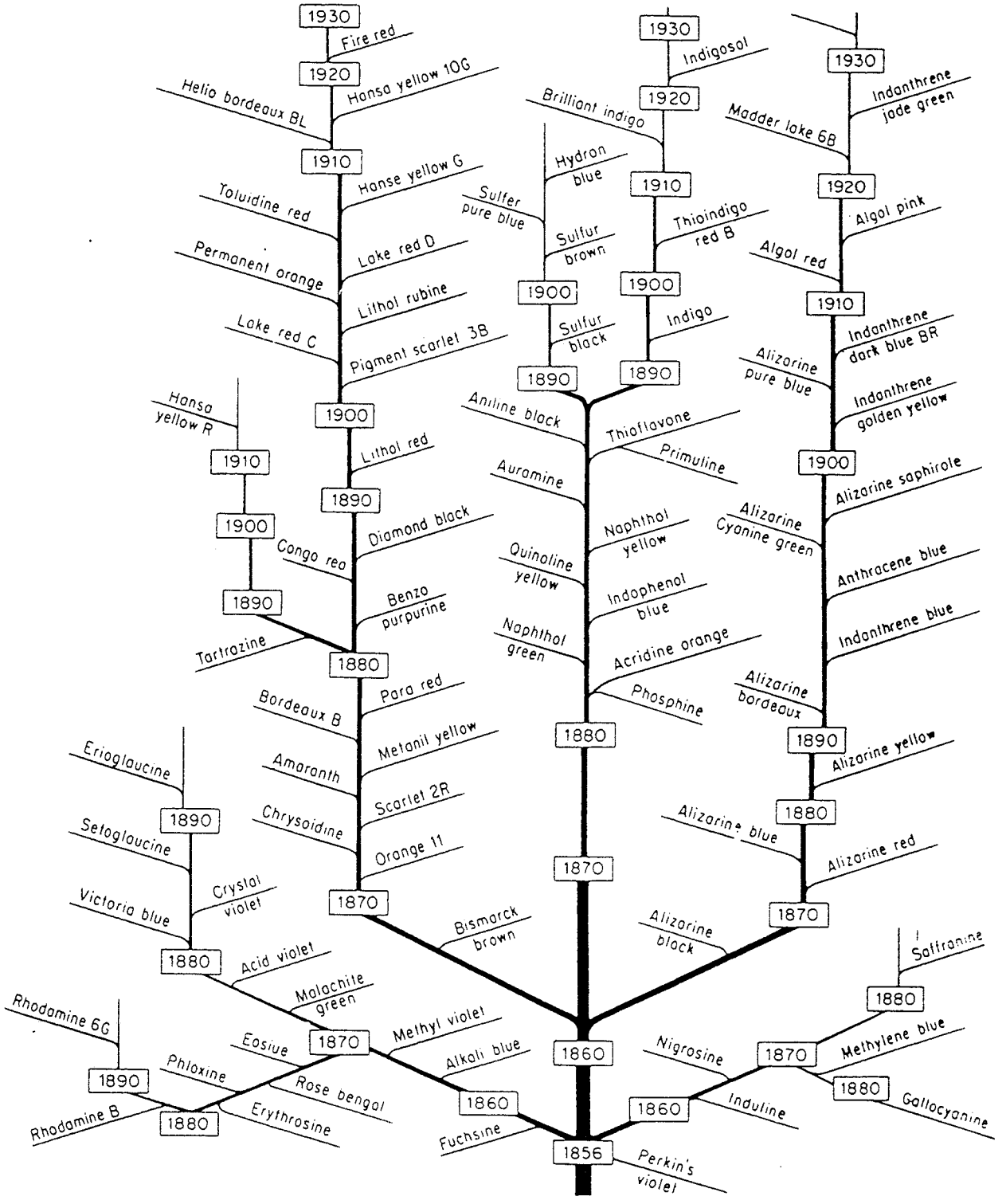


Fig. 39.5. Significant developments in organic color chemistry. *(Interchemical Corp. and John Wiley and Sons, Inc.)*

textiles), are: $-NH_2$, $-OH$, $-NR_2$, $-COOH$, and $-SO_3H$. It is not a coincidence that these are salt-forming materials; $-NH_2$ and $-NR_2$ cause solubility in acid; $-OH$, $-COOH$, and $-SO_3H$ cause solubility in basic solutions.

Figures 39.6, 39.7, and 39.8 are helpful in visualizing the relationship between precursors, intermediates, and a few simple dyes.

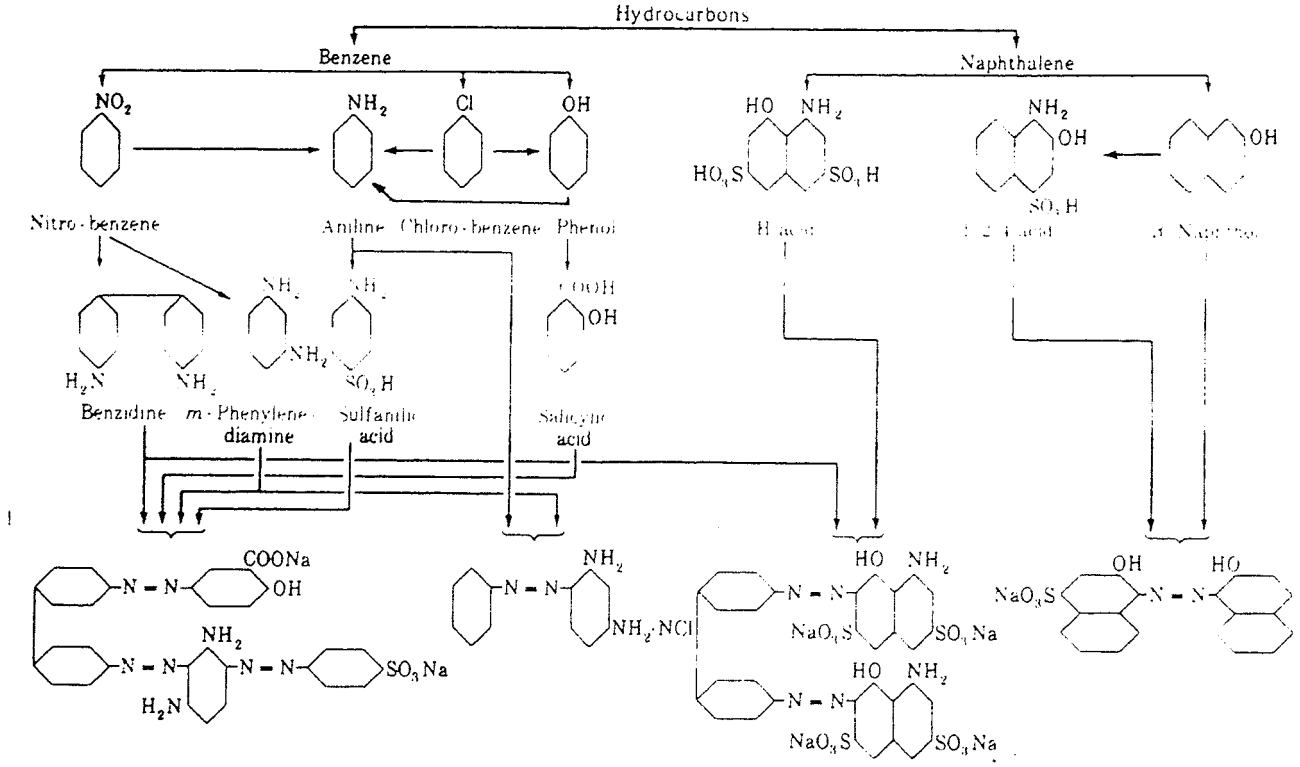


Fig. 39.6. Relationship of hydrocarbons, intermediates, and some azo dyes.

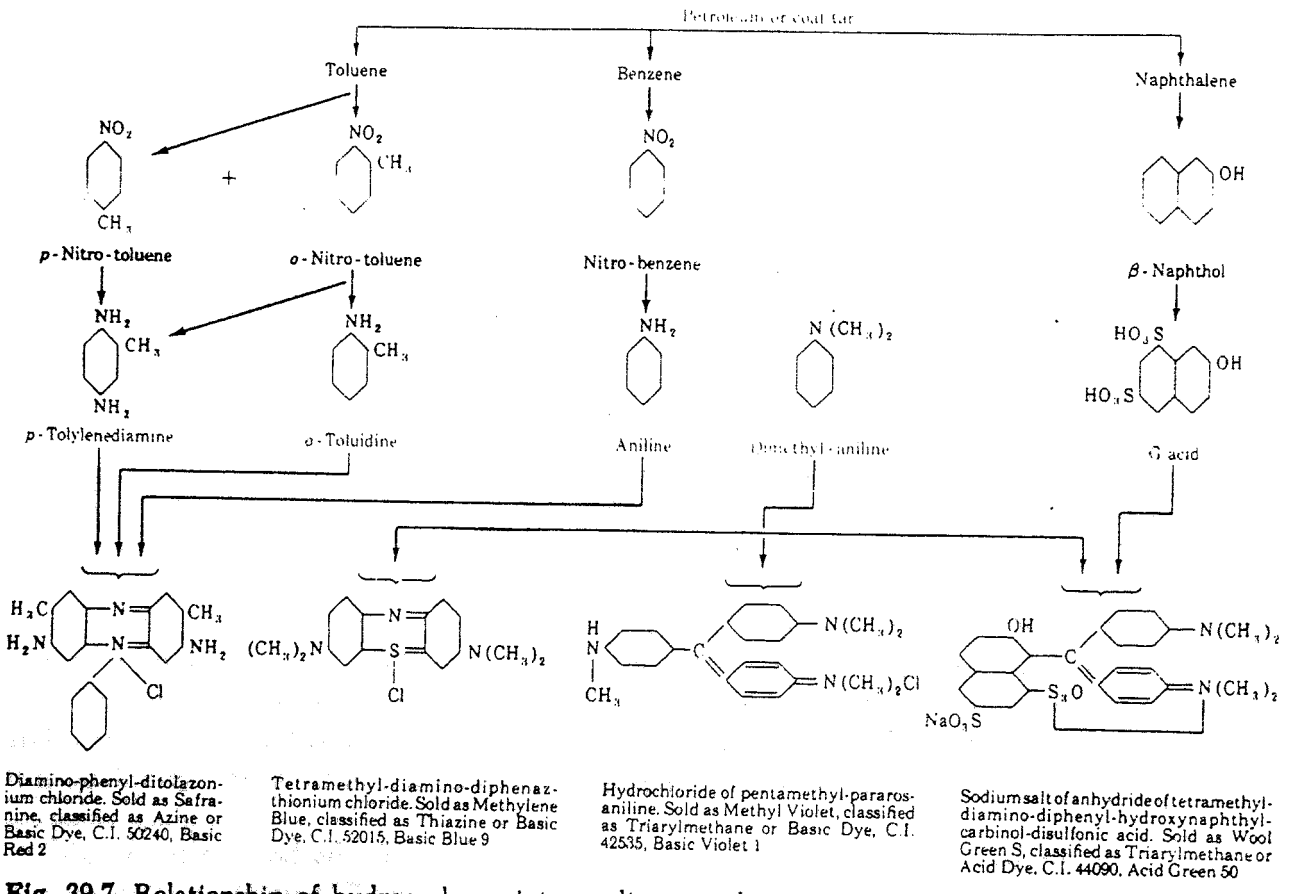


Fig. 39.7. Relationship of hydrocarbons, intermediates, and some azine, thiazine, and triarylmethane dyes.

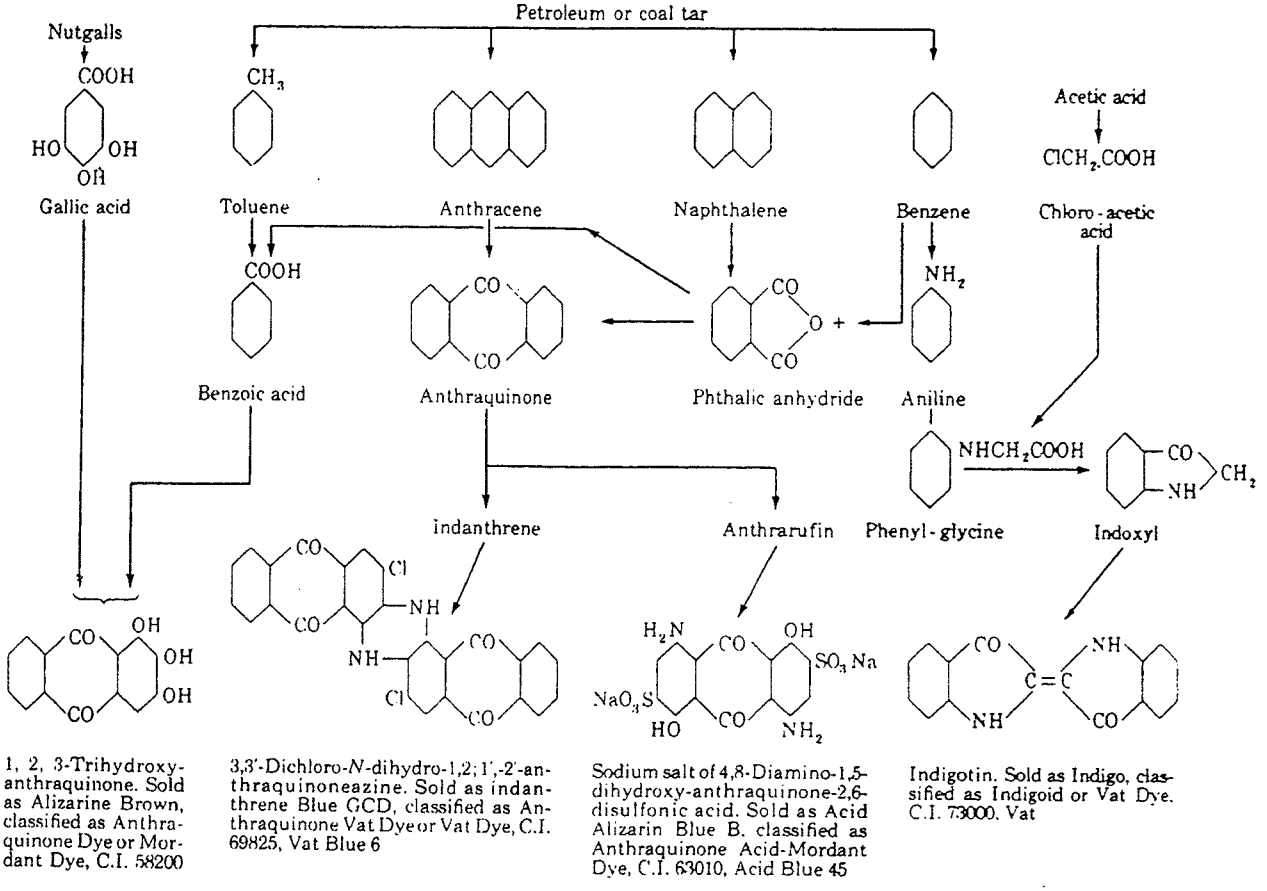


Fig. 39.8. Relationship of hydrocarbons, intermediates, indigo, and some anthraquinone dyes.

CLASSIFICATION OF DYES. It is possible to classify dyes by using an ingenious system[13] devised some years ago by the Society of Dyers and Colourists and published as the *Colour Index*. This is undoubtedly the most important book available concerning dyes. The *Colour Index* classifies dyes according to a dual system. An assigned number defines the chemical class and a generic name identifies the usage of application. Some manufacturers append a trivial or trade name. Notice in Figs. 39.6 and 39.9: Chrome blue-black U (a trade name), CI 15705 (Numbers 11,000 to 19,999 are reserved for monoazo dyes), Mordant black 17 (an azo dye applied as a mordant, No. 17 in the list of this type). The Colour Index recognizes 26 types of dyes by chemical classification: (1) nitroso, (2) nitro, (3) mono-, dis-, tris- and poly-azo, (4) azoic, (5) stilbene, (6) carotenoid, (7) diphenylmethane (ketone imine), (8) triarylmethane, (9) xanthene, (10) acridine, (11) quinoline, (12) methine and polymethine, (13) thiazole, (14) indamine and indophenol, (15) azine, (16) oxazine, (17) thiazine, (18) sulfur, (19) aminoketone, (20) hydroxyketone, (21) anthraquinone, (22) indigoid, (23) phthalocyanine, (24) natural organic coloring matters, (25) oxidation bases, and (26) inorganic coloring matters.

It is convenient to use the application classification used by the U.S. International Trade Commission for application classes: (1) acid dyes, (2) azoic dyes, (3) basic dyes, (4) direct dyes, (5) disperse dyes, (6) fiber-reactive dyes, (7) fluorescent brightening agents, (8) food, drug, and cosmetic colors, (9) mordant dyes, (10) solvent dyes, (11) sulfur dyes, and (12) vat dyes. It is obviously impractical in a book of this size to discuss all the combinations of properties

[13]*Colour Index*, 3d ed., 5 vols., Society of Dyers and Colourists, Bradford, England, and American Association of Textile Chemists and Colorists, Lowell, Mass., 1971.

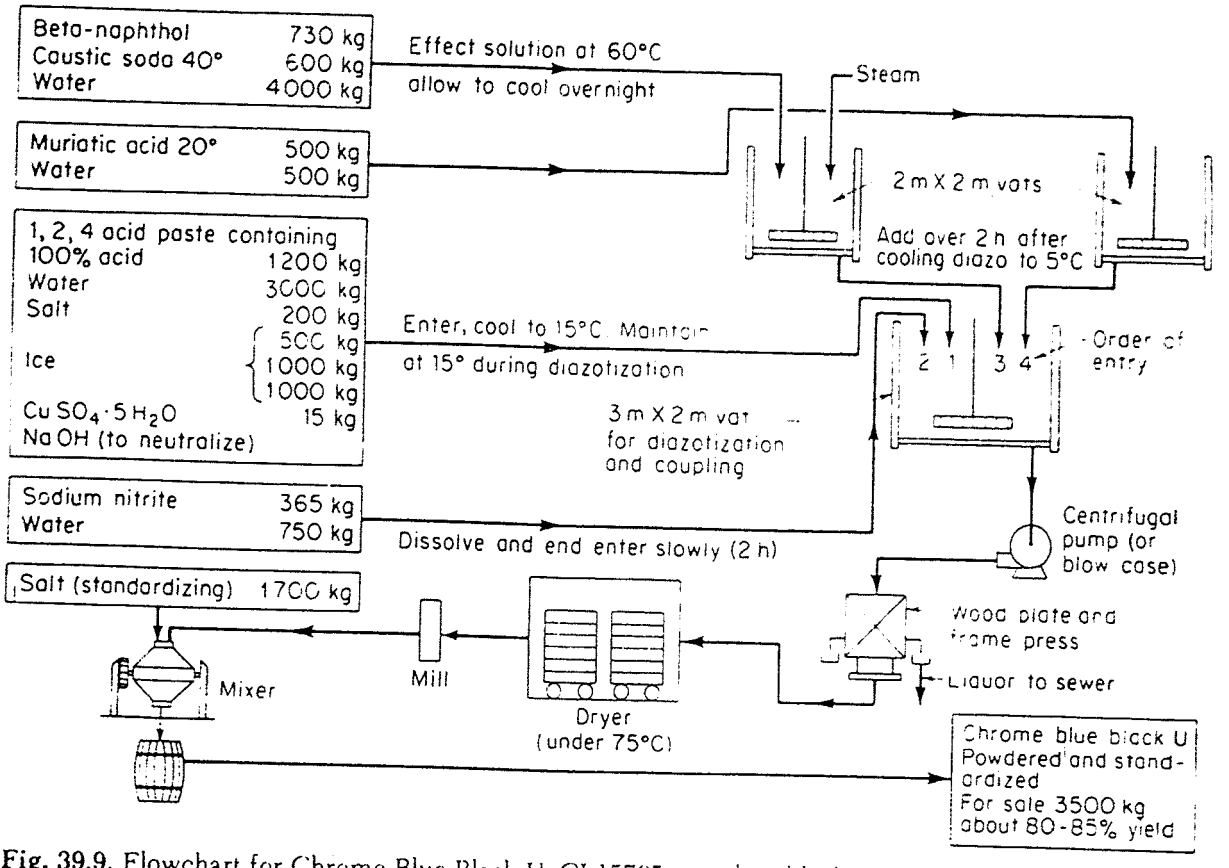


Fig. 39.9. Flowchart for Chrome Blue Black U, CI 15705, mordant black 17. A monoazo or chrome dye; batch = 5 kg-mol.

and chemical compositions possible. Note, however, that six classes form the bulk of the market, so it is possible to concentrate on them. Table 39.3 shows the size and value of the markets. They are: acid, basic, direct, disperse, reactive, and vat dyes. Large compendiums[14] make it possible to obtain data on those omitted here.

The significance of the various application classes are as follows:

Acid dyes. These derive their name from their insolubility in acid baths. They are used for dyeing protein fibers such as wool, silk, and nylon; also leather and paper. Usually they are azo, triaryl methane, or anthraquinone complexes.

Azoic dyes. These "ice colors" are made right on the fiber by coupling diazotized materials while in contact with the fibers. Low temperature keeps the diazonium compound from decomposing until ready to couple. These are brilliant and long-lasting and are used primarily for printing on cotton.

Basic dyes. Basic dyes are mostly amino and substituted amino compounds soluble in acid and made insoluble by the solution being made basic. Most are triarylmethane or xanthenes. These can be used to dye wool or cotton with a mordant, but are usually used for duplicator inks, carbon paper, and typewriter ribbons. In solvents other than water, they form writing and printing inks.

Direct dyes. Direct dyes are used to dye cotton directly, that is, without the addition of a mordant. They are also used to dye union goods (mixed cotton, and wool, or silk). These are generally azo dyes, and their solubility in the dye bath is often reduced by adding salt.

[14]Venkataraman, op. cit.; ECT, op. cit.; Kent, *Riegel's Industrial Chemistry*, Reinhold, New York, 1962.

Table 39.3 Comparison of U.S. Production of Dyes, by Classes of Application

Class of Application	1972		1980	
	Production, 10^3 kg	Value, 10^6 $	Production, 10^3 kg	Value, 10^6 $
Acid	13,518	71.7	11,640	115
Basic (classical and modified)	8,181	48.9	6,634	71.1
Direct	17,124	59.2	14,191	83.3
Disperse	18,149	107.6	21,236	178.1
Fiber reactive	1,681	15.6	2,605	36.0
Fluorescent brightening agents	12,419	38.3	17,245	60.4
Food, drug, and cosmetic colors	2,111	19.8	2,761	48.4
Mordant	666	2.6	186	1.9
Solvent	5,667	22.3	4,829	28.9
Vat	25,064	63.3	18,286	120.4
All others	10,461	16.3	11,909	46.9

SOURCE: *Synthetic Organic Chemicals*, U.S. International Trade Commission.

Some are developed on the fiber by forming the diazonium salt on the cloth, then coupling to increase insolubility. β-Naphthol is the most common developing agent.

Disperse dyes. Modern synthetics (cellulose acetate, plastics, polyesters) are difficult to dye. Disperse dyes are applied as very finely divided materials which are adsorbed onto the fibers with which they then form a solid solution. Simple, soluble azo dyes can be used, but insoluble anthraquinone colors are best and most common. Both penetrate the fiber. The ethanolamine group $-NHCH_2CH_2OH$ is commonly found in this group and aids both in dispersion and absorption.

Fiber-reactive dyes.[15] These dyes react to form a covalent link between the dye and the cellulosic fiber which they are customarily used to dye. This produces goods of outstanding wash-resistance. Cotton, rayon, and some nylons are dyed by this, the newest type of dyestuff to be invented (1956).

Fluorescent brightening agents.[16] Everyone knows what is meant by white, but its accurate definition and description prove to be quite elusive. "Bluing" has been used for a very long time to make yellowish laundry appear "whiter." Greater brilliance can be obtained with soap, textiles, plastics, paper, and detergents by the addition of these "optical brighteners." They absorb ultraviolet light and emit bright blues, which gives greatly improved whiteness. Brightners are stilbenes with some oxazoles and triazoles as well.

Reflecting pigments such as titanium dioxide are often added to paper to improve its whiteness. Brighteners are helpful in improving the appearance of recycled paper.

Food, drug, and cosmetic colors.[17] These currently consist of only 52 dyes, a carefully controlled group of materials regulated by the U.S. Food and Drug Administration. Purity and safety are rigidly monitored; some dyes are "listed" and some are "certified." Listed ones

[15]Hildebrand, Fiber Reactive Dyestuffs, *CHEMTECH* 8 (4) 224 (1978).

[16]Consumer Demand Spurs Brightener Use, *Chem. Eng. News* 43 (15) 37 (1965); Blanchard, Harper, Gautreaux, and Reid, Optical Brightener Adsorption by Polymer-Treated Fabrics, *CHEMTECH* 1 (3) 181 (1971).

[17]Greene, Food Dye Users See Red over FDA Color Bans, *Chem. Eng.* 84 (2) 84 (1977); These Colorants Can't Hurt You, *Chem. Week* 120 (17) 65 (1977).

have met safety standards; certified ones have the actual batch identical with an approved original standard. Considerable controversy surrounds several currently approved colors, and it seems probable that the number will be reduced still farther. An interesting development is the linking of certain dyes to polymer chains, thus causing them to pass through the digestive tract unchanged. Several such colors are currently undergoing tests to determine their chronic effects. Approved colors include anthraquinones, azos, and indigoids.

Mordant dyes (and lakes). Some dyes combine with metallic salts (mordant means bitter) to form highly insoluble colored materials called lakes. These materials are usually used as pigments. If a cloth made of cotton, wool, or other protein fiber is impregnated with an aluminum, chromium, or iron salt and then contacted with a lake-forming dye, the metallic precipitate forms in the fiber, and the colors become far more resistant to light and washing. Substituent groups such as $-OH$ and $-COOH$ attached to azo or anthraquinone nuclei are capable of reaction with metals to form mordant dyes.

Solvent dyes. Some simple dyes are soluble in alcohols, chlorinated hydrocarbon solvents, or liquid ammonia and there appears to be considerable promise in dyeing the difficult to dye synthetics, polyesters, polyacrylates, and triacetates, from such solutions. Perchloroethylene has been the preferred solvent to date. Such technology would greatly decrease the problem of removing unabsorbed dye from outfall waters, which can be very troublesome to dyers. The system has had some success in Europe. Because new dyeing machines must be developed to handle the volatile solvents used, and because the designs to contain the vapors represent considerable change from present machines, dyers in the United States have not shown a great deal of interest. Solvent, sometimes called spirit-soluble, dyes are usually azo, triarylmethane bases, or anthraquinones. They are used to color oils, waxes, varnishes, shoe polishes, lipsticks, and gasolines.

Sulfur dyes (sulfide dyes). These are a large, low-cost group of dyes which produce dull shades on cotton. They have good fastness to light, washing, and acids, but are very sensitive to chlorine or hypochlorite. The chromophore is complex and not well-defined; it is made by reacting sulfides and polysulfides with chlorinated aromatics. Sulfur dyes are usually colorless when in the reduced form in a sodium sulfide bath but gain color on oxidation. They have been used for a long time.

Vat dyes. These have chemical structures that are highly complex and most are derivatives of anthraquinone or indanthrene. On reduction in solution, they become alkali-soluble and colorless, and are called leuco vats. The colorless compounds are used to impregnate cotton fibers, which are then treated with an oxidant or exposed to air to develop the colors. Vat dyes are expensive, but are used for fabrics in severe service with frequent washing, such as men's shirts. Some vats are supplied as pastes for printing. The pastes contain sodium hydrosulfite and an aldehyde reducing agent. They can be printed on cloth, then developed by passing through an oxidizing bath containing sodium dichromate or perborate. The production of some vat dyes is described in Fig. 39.10.

The best known dye of the class is indigo, which has a fascinating history.[18] It was originally obtained from European woad or Indian indigo (and was for a time grown as a cash crop in the United States). It is now made synthetically, see Fig. 39.11, and is one of the most popular colors in the world. When used for dyeing wool, it makes dark (navy) shades with excellent fastness properties. As a dye for cotton denim, its lack of fastness seems to be prized as a fad. Several modified indigos, such as thioindigo, give very bright shades with good fastness when used on rayon.

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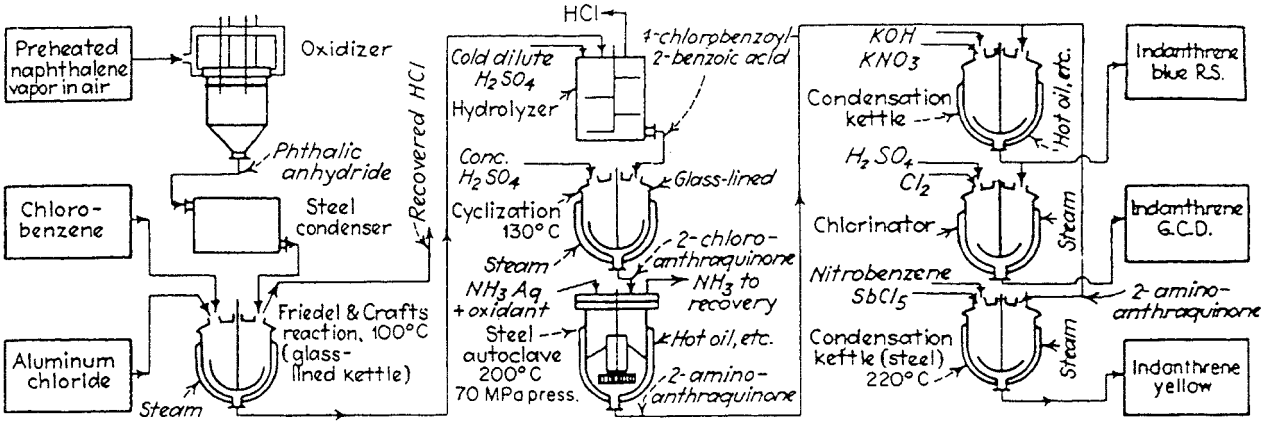
[18] Baumler, *A Century of Chemistry*, Econ Verlag, Dusseldorf, 1968.



Materials (in kilograms) to produce simple vat dyes.

2-CHLOROANTHRAQUINONE, 235 KG		2-AMINOANTHRAQUINONE, 200 KG	
Phthalic anhydride	148	2-Chloroanthraquinone	235
Chlorobenzene (80% rec'd)	600	NH_3 (28%)†	1500
Aluminum chloride	300		
H_2SO_4 (100%)	1500		
INDANTHRENE YELLOW G, C.I. 70600, VAT YELLOW 2		**INDANTHRENE BLUE R.S. C.I. 69800, VAT BLUE 4, 60–65 KG 100% DYE**	
2-Aminoanthraquinone	200	2-aminoanthraquinone	200
Nitrobenzene*	2000	Caustic potash	1000
Antimony pentachloride	700	KNO_3 (or K-chlorate)	40
INDANTHRENE BLUE G.C.D., C.I. 69810, VAT BLUE 14, ABOUT 100% DYE			
Indanthrene blue R.S.	100		
H_2SO_4 (93%)	1200		
$FeSO_4$	90		
Cl_2	25		

Recovered as aniline or as nitrobenzene.

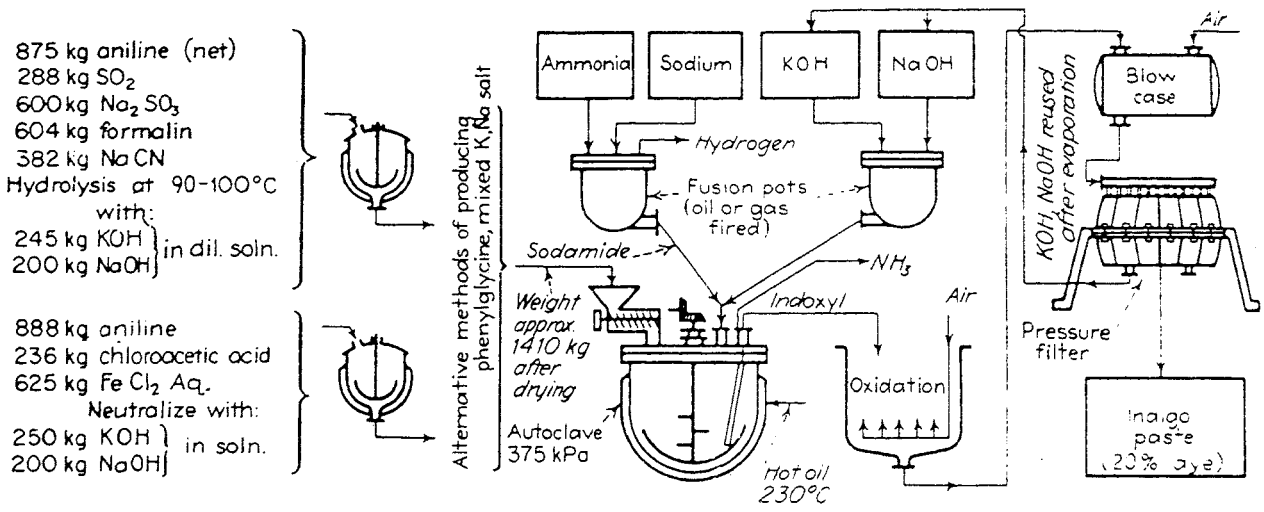
†90% recoverable.

Fig. 39.10. Outline flowchart for simple vat dyes, not detailed.

MANUFACTURE OF DYES. Because the chemistry is relatively easy (although the quality control is not) and so many reactions have small heat effects and can be run in simple open vessels, at one time many dyes were synthesized in wooden vats. The reaction between sodium nitrite and an amine, if carried out at ice temperature, produces a highly reactive ionized diazonium salt which will react (couple) rapidly with another molecule to form a body, which is usually colored, in nearly quantitative yield. Typical reactions are:

$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

$$RNH_2 + HNO_2 \rightarrow \underset{\text{Aryl diazonium chloride}}{RN_2^+Cl^-} + 2H_2O \quad \begin{array}{ll} \text{if R = benzene,} & \Delta H = -94.5 \text{ kJ} \\ \text{if R = } \alpha\text{-naphthylamine} & \Delta H = -103.9 \text{ kJ} \end{array}$$



In order to produce 1 t of 100% indigo or 5 t 20% paste, the following materials (in kilograms) are required. NOTE: Yields 80–82 percent on aniline; KOH, NaOH, NH_3 recovered and reused.

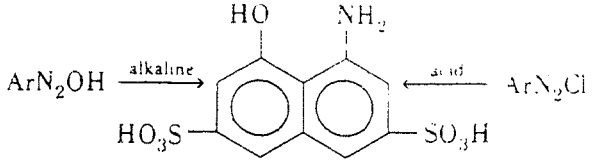
Phenylglycine (K,Na)	1550	Sodium	430
KOH (recovered)	1525	Ammonia	315
NaOH (recovered)	1200		

Fig. 39.11. Outline flowchart for the production of indigo.

COUPLING REACTIONS

$$RN_2^+Cl^- + ArOH \rightarrow RN{=}NArOH + HCl$$
$$\text{or } ArNH_2 \rightarrow RN{=}NArNH_2 + HCl$$

Coupling follows definite rules[19] determined by electronic configuration, and these permit isomeric structural differences to be exploited. Phenols, naphthols, and corresponding amines are the substances usually coupled. Polyfunctional intermediates can have nitro groups reduced after coupling and be coupled again. The pH of the bath may also determine the point of coupling. Consider the common intermediate, H-acid. (In the shorthand used for the naphthalene intermediates, known as NSSO 1368, S = SO_3H, N = NH_2, and O = OH, and the usual numbering system is used for the naphthalene.) It couples as follows:

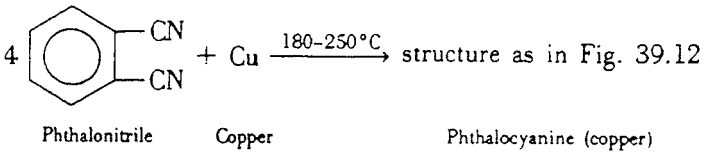


The wood vat has been almost entirely replaced by stainless steel, enameled steel, plastic, and rubber- and carbon-block–lined units, largely because of the ease of cleaning, which makes it unnecessary to reserve a vat for each color processed. There has also been a fair amount of automation, but Figs. 39.9 and 39.10 show typical steps in the manufacture of dyes. Great strides have been made in protecting the workers from toxic intermediates, increasing cleanliness as a whole, and standardizing colors for guaranteed reproducible

[19]Rys and Zollinger, *Fundamentals of the Chemistry and Application of Dyes*, Wiley, New York, 1972; Venkataraman, op. cit.; ECT, 3d ed., vol. 8, 1979, p. 159 ff; Abrahart; *Dyes and Their Intermediates*, Edward Arnold, London, 1977.

results. The industry still remains labor intensive, subject to abrupt changes in tastes for colors, and loaded with the burden of carrying a large inventory at a time of high interest rates. Customer service has also been a heavy load on the industry.

Complexity of dye structure does not necessarily indicate complexity of manufacture. Copper phthalocyanine (Fig. 39.12) is a good case in point. This is a highly chlorinated dye and is CI 74260, pigment green 7. There are 15 to 16 chlorine atoms, probably randomly distributed, per phthalocyanine unit. Phthalocyanines form only blues and greens, but their colors are extremely stable and give pigments used in artist's colors, printing inks, surface coatings, paper, floor coverings, and rubber. They are so stable that they have been used as high-temperature lubricants for space vehicles. They are made as follows:



NATURAL DYES. Most early dyes were animal-derived or vegetable extractives. Madder, indigo, Turkey red, Tyrian purple, picric acid, butternut juice, and walnut juice are some dyes known before chemistry took over, and some of them are quite good, but the good ones are usually extremely expensive to produce and quality control is virtually nonexistent. All extractives have disappeared from commercial use except logwood, CI 75290, natural black 1, which is the extract from the wood of a Central American tree.

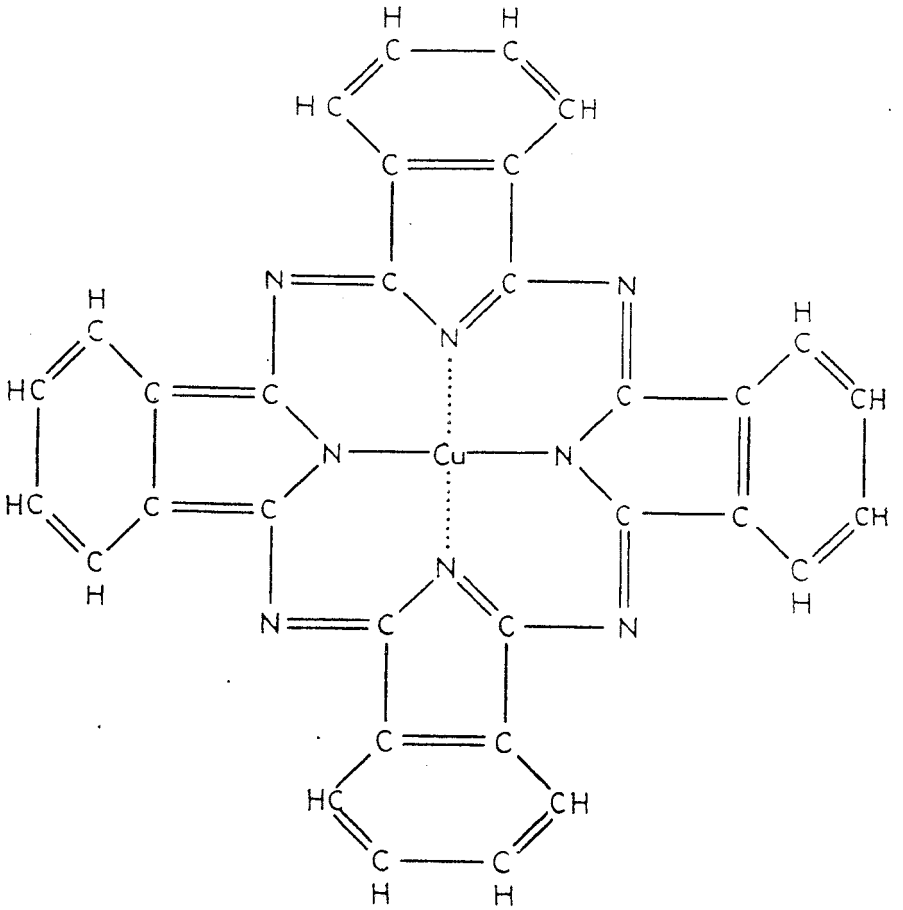


Fig. 39.12. Copper phthalocyanine basic structure.

INORGANIC COLORING MATTERS. Inorganic materials used as pigments are considered in Chap. 24. Some khaki for tents and similar outdoor use is still made by soaking the cloth in ferrous sulfate or acetate. On drying, or the addition of an alkali, the hydroxide is formed, which is oxidized to the more highly colored ferric hydroxide with bleach.

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MINISTRY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF

TECHNICAL AND VOCATIONAL EDUCATION

ChT – 03014

CHEMICAL TECHNOLOGY I

B.Tech (First Year)

Chemical Engineering

PART 1

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Chapter 1

Water Conditioning and Environmental Protection

Water conditioning and wastewater treatment have long been essential functions of municipalities. However, the importance of suitably preparing water for the chemical industry is now fully recognized. Industrial wastewaters present a complex and challenging problem to the chemical engineer. Besides moral and community considerations, laws prohibiting and limiting the pollution of streams and air require these problems to be considered as a necessary operating expense. Although the solution is specific with each industry (indeed, almost with each plant or factory), a few general principles may be observed: increasing reuse of wastewaters, control of pollution and, if feasible, recovery of by-products at their source to lessen the expense of treatment, and lagooning of wastes to keep pollution at a minimum level or to effect a saving in neutralization costs.

As is well known, the quality and the quantity of available water are very important in choosing the location of a chemical plant. Both the surface water and the groundwater should be considered. The latter is usually more suitable for cooling purposes because of the fairly constant temperatures during the summer and winter, but such water is generally harder, may cause scale, which may interfere with heat transfer. The impurities contained in water vary greatly from one section of the country to another. Hard waters are those containing objectionable amounts of dissolved salts of calcium and magnesium. These are usually present as bicarbonates, chlorides, sulfates, and nitrates. These salts give insoluble precipitates with soap, and calcium sulfate, carbonate, and silicate form clogging scales with low thermal conductivity in boilers. Magnesium silicate, as well as calcium carbonate, may reduce heat transfer in process heat exchangers.

Although, on an average day, 1.6×10^{10} m^3 of water falls on the United States (76 cm/year average), of which 70 percent is recycled to the atmosphere by evaporation or transpiration of plants, the increasing growth of population and of industry makes for local shortages. The amount of water used in the United States in 1960 amounted to 1.18×10^9 m^3/day and in 1980, 2.11×10^9 m^3/day. The total supply of fresh water available in the United States has been estimated at 2.46×10^9 m^3/day, so it is obvious that demand is rapidly overtaking the supply.

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[1] *Water Quality and Treatment, A Handbook of Public Water Supplies*, American Water Works Assoc., 3d ed., McGraw-Hill, New York, 1971. Chanlett, *Environmental Protection*, McGraw-Hill, New York, 1973.

The problems[2] of quantity, quality, reuse, and pollution are complex and usually require expert study to decide between alternative sources of water and optimum treatment to minimize total cost of use. The decision generally depends on the use, whether for power generation, heating, cooling, or actual incorporation into a product or its manufacturing process.

Hardness is usually expressed in terms of the dissolved calcium and magnesium salts calculated as calcium carbonate equivalent. Water hardness may be divided into two classes: *carbonate* and *noncarbonate*, known as *temporary* and *permanent*. Temporary hardness can usually be greatly reduced by heating; permanent hardness requires the use of chemical agents. Carbonate, or temporary hardness, is caused by bicarbonates of calcium and magnesium; noncarbonate, or permanent hardness, is due to the sulfates and chlorides of calcium and magnesium. In addition to hardness, varying amounts of sodium salts, silica, alumina, iron, or manganese may also be present. The total dissolved solids may range from a few parts per million in snow water to several thousand parts per million in water from mineral springs. A water that contains even 1000 parts per million dissolved solids is considered to be a relatively poor quality water even though it is 99.9% pure. In the United States hardness is expressed as if all the hardness were due to calcium carbonate. The common units used in expressing water analyses are parts per million (ppm), grains per gallon (gr/gal), and milligrams per liter (mg/L). One grain per gallon is equivalent to 17.1 ppm and 17.1 mg/L. Other water impurities that may be present are suspended insoluble matter (classed usually as turbidity), organic matter, color, and dissolved gases. Such gases are free carbon dioxide, oxygen, nitrogen, and, in sulfur waters, hydrogen sulfide.

Approximately 5×10^8 m^3 (133×10^9 gal) of municipal wastewater is reused for agriculture, cooling and process water, and nonpotable domestic applications. Industry may withdraw large quantities of water from the original source and use it in varied ways, but it actually consumes relatively little,[3] so that most of the water is returned to the source for reuse by others. The U.S. Department of Commerce has estimated that the average chemical process industry plant that had recycle rates of 2:1 to 5:1 just a few years ago is expected to reach 1:1 (pulp and paper), 27:1 (chemicals), and 40:1 (petroleum refining) by the year 2000. The recycle rate is the ratio of gross water use to intake. In many areas, treated sewage effluent is of a better quality than the natural water supply and, with improved waste treatment, industrial reuse becomes more and more feasible. Roughly 70 percent of all industrial water is used for cooling. Industrial reuse helps to reduce the chemical, thermal, and resultant biological stream pollution and brings the handling of water more under the direct control of the plant manager. Table 3.1 shows the trends in industrial reuse.

WATER CONDITIONING

Water conditioning must be adapted to the particular use for which the water is designed, and problems should be referred to the experts in this field. The use of elevated pressures

[2]*American Water Works Association Water Control and Treatment*, 3d ed., McGraw-Hill, New York, 1971; Spiegler, *Salt Water Purification*, Plenum, New York, 1977.

[3]Water Reuse: A Trickle Becomes a Torrent, *Chem. Eng.* 85 (10) 44 (1978); *Water Reuse Studies*, API Publication 949, Washington, D.C., Aug. 1977; Foster and Barkely, *Water Reuse in the Southwest*, AIChE Symposium Series, vol. 73, no. 166, p. 183 1977; Holiday, Conserving and Reusing Water, *Chem. Eng.* 89 (8) 118 (1982).

Table 3.1 Water-Use Patterns in the United States* (10^6 m^3/day)

	Gross Use	Intake	Consumption	Total Discharge
1975				
Pulp and paper	110	38	3.8	34
Petroleum	95	19	3.8	15
Chemical and allied products	166	80	3.8	76
Total manufacturing	580	260	3.6	235
1985				
Pulp and paper	163	26	7.5	15
Petroleum	110	7.5	3.8	3.8
Chemical and allied products	310	23	7.5	15
Total manufacturing	860	102	38	64
2000				
Pulp and paper	261	23	19	3.8
Petroleum	155	3.8	3.8	>2
Chemical and allied products	602	23	15	3.8
Total manufacturing	1404	87	64	2.3

*Data are rounded.

SOURCE: U.S. Dept. of Commerce

(17.2 MPa and higher for steam generation) requires the employment of extremely carefully purified boiler feedwater. Each industry has its special water-conditioning requirement; e.g., laundries require zero hardness to prevent the precipitation of calcium and magnesium soap on clothes. Calcium, magnesium, and iron salts cause undesirable precipitates with dyes in the textile industries and with the dyes in paper manufacture.

HISTORICAL. In this country an abundance of fairly soft water has long been available from surface supplies of the industrial Northeast. Cities such as New York and Boston obtain comparatively soft water from rural watersheds over igneous rocks. However, as the Middle West and the West were developed, it became necessary to use the harder water prevailing in many areas, particularly those rich in limestone. This hard water needs to be softened for many uses. Furthermore, as the advantages of really soft water are recognized, more and more fairly soft waters are being *completely softened* for laundries, homes, textile mills, and certain chemical processes. Thomas Clark of England, in 1841, patented the lime process for the removal of carbonate, or temporary hardness, followed by Porter, who developed the use of soda ash to remove the noncarbonate, or permanent, hardness of water. In 1906, Robert Gans, a German chemist, applied zeolites to commercial use for water-softening purposes. Only since the 1930s has softening been extended to municipal supplies to any appreciable extent. Figure 3.1 shows in a general way the variations in hardness of waters.

METHODS. The purification and softening of water may be accomplished by different methods, depending on the prospective use. *Softening* is the term applied to processes which remove or reduce the hardness of water. *Purification*, as distinguished from softening, usually refers to the removal of organic matter and microorganisms from water. *Clarification* may be very important and may be combined with cold-water softening by precipitation.

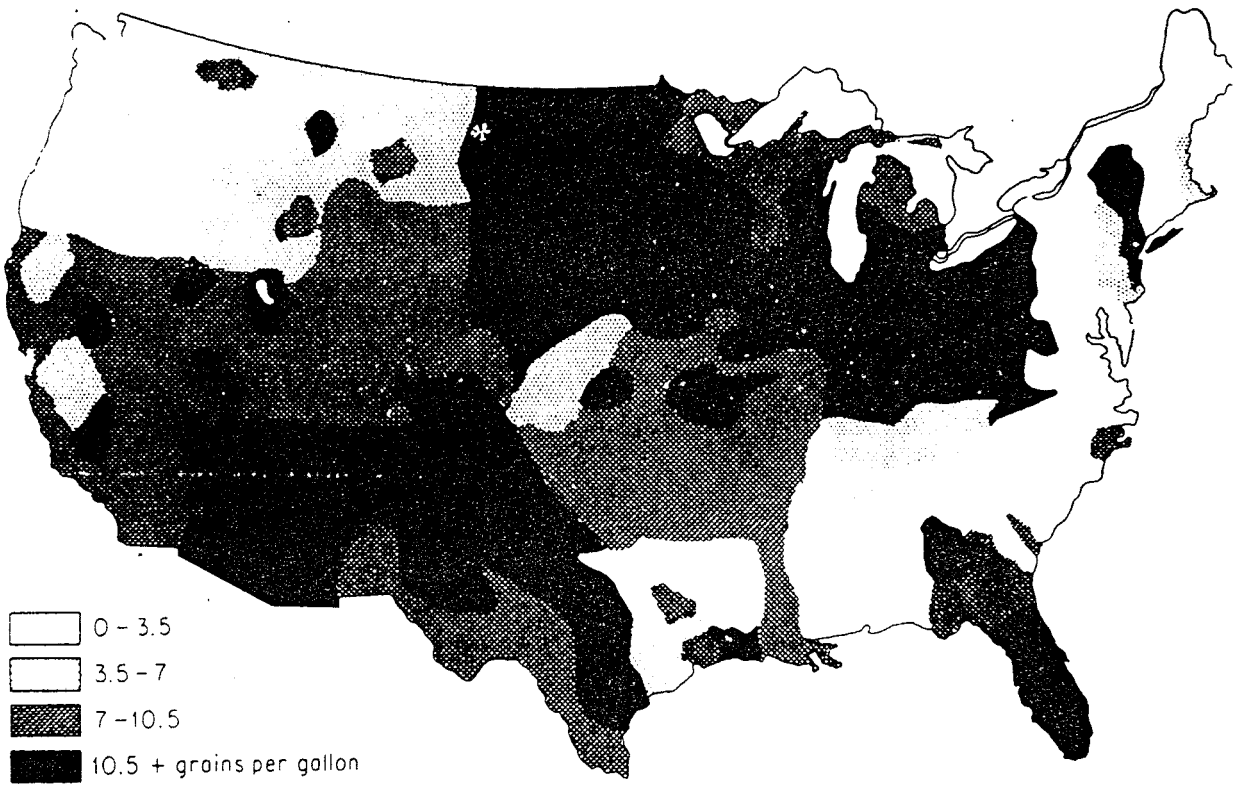


Fig. 3.1. A hard-water map of the United States shows that few parts have soft water (white areas). Most of the country has water of varying hardness (gray and black areas).

Ion Exchange. In 1852, Way discovered that the removal of ammonia from aqueous liquids passing through certain soils was really an exchange with the calcium of a particular type of silicate occurring in the soils. The real stimulus for organic exchange resins came when Adams and Holmes[4] published their paper on purely synthetic organic exchange resins and described anion-exchange resins. Now ion exchange has become a valuable chemical conversion process. Its utilization on a large industrial scale is widespread, including the commercial production of demineralized water having low electrical conductivity. Ion exchange is really a chemical reaction in which mobile hydrated ions of a solid are exchanged, equivalent for equivalent, for ions of like charge in solution. The solid has an open fishnetlike structure, and the mobile ions electrically neutralize charged, or potentially charged, groups attached to the solid matrix, called the ion exchanger. Cation exchange occurs when the mobile, positively charged cation fixed to the negatively charged fixed group of the ion exchanger, exchanges for another cation in the solution. Likewise, anion exchange occurs when the mobile, negatively charged anion attached to the positively charged fixed group on the ion exchange resin is exchanged for another anion in the solution.[5]

The first products used industrially for ion exchange were naturally occurring inorganic zeolites, such as aluminum silicates, which have very low exchange capacity per cubic meter of the material. The next improvement was the introduction of organic ion exchangers which

[4]*Soc. Chem. Ind. London Chem. Eng. Group Proc.* 54 1-6T (1935); Arden, *Water Purification by Ion Exchange*, Plenum, New York, 1968.

[5]***McGraw-Hill Encyclopedia of Science and Technology,*** vol. 14, McGraw-Hill, New York, 1977, p. 457.

have very high exchange capacity per cubic meter of material. The next improvement was the introduction of organic ion exchangers made from sulfonated natural products such as coal, lignite, and peat. However, most high-capacity ion-exchange resins are based upon polystyrene-divinylbenzene (SDVB). Over 80 percent of ion-exchange resins are used for the treatment of water. However, the nonwater uses are of great importance and are growing. The literature covering all the versatile applications of ion exchanges is extensive.[6] They can be chosen to remove and purify, for example, uranium, yttrium, or streptomycin (Chap. 40) from dilute aqueous solutions, or to remove impurities from aqueous solutions, as in sugar syrup to improve crystallization, or in food technology, or for catalysts, or simply to dry nonpolar solvents.

Sodium-cation-exchange process is the most widely employed method for softening water.[7] During the softening process, calcium and magnesium ions are removed from hard water by cation exchange for sodium ions. When the exchange resin has essentially removed the calcium and magnesium ions to the limit of its capacity, the resin is regenerated to the sodium form with a salt solution in the pH range of 6 to 8. The exchange capacity of polystyrene resins is 650 kg/m^3 when regenerated with 250 g of salt per kilogram of hardness removed. The sodium or hydrogen-cycle cation exchangers for water treatment are usually of the styrene-divinylbenzene sulfonated synthetic resin type. This type is exceptionally stable at high temperatures (up to 150°C) and over the wide pH range of 0 to 14. In addition, it is very resistant to oxidizing conditions. The total exchange capacity is up to 925 kg of $CaCO_3$ per cubic meter of ion exchanger with a hydrogen cycle and up to 810 kg of $CaCO_3$ per cubic meter with a sodium cycle. The usual practical operating capacities are not so high.

The symbol R represents the cation-exchanger radical in the following reactions for softening:

$$\begin{Bmatrix} Ca \\ Mg \end{Bmatrix} \begin{matrix} (HCO_3)_2 \\ SO_4 \\ Cl_2 \end{matrix} + 2NaR \rightarrow \begin{Bmatrix} Ca \\ Mg \end{Bmatrix} R_2 + Na_2 \begin{matrix} (HCO_3)_2 \\ SO_4 \\ Cl_2 \end{matrix}$$

Calcium and/or magnesium	Bicarbonate, sulfate, and/or chloride	Sodium cation exchanger	Calcium and/or magnesium cation exchanger	Sodium	Bicarbonate, sulfate and/or chloride
(soluble)		insoluble	(insoluble)		soluble

When the ability of the cation-exchange bed to produce completely softened water is exhausted, the softener unit is temporarily taken out of service, backwashed to cleanse and hydraulically reclassify the resin particles in the bed; regenerated with a solution of common salt (sodium chloride), which removes the calcium and magnesium in the form of their soluble chlorides and simultaneously restores the cation exchanger to its sodium state; rinsed free of these soluble by-products and the excess salt, and then returned to service ready to soften another equal volume of hard water. The regeneration reactions may be indicated as follows:

[6]ECT, 3d ed., vol. 13, 1981, p. 678; Walton, Ion Exchange, *Anal. Chem.* 42 (5): 86 (1970).

[7]Gold and Calmon, *Ion Exchange, Present Status, Needs and Trends*, AIChE Symp. Ser., vol. 76, no. 192, p. 60, 1980, a review with 106 references.

using salt (or H_2SO_4 on a hydrogen cycle):

$$\begin{matrix}\text{Ca}\\\text{Mg}\end{matrix}\Big\} R_2 + 2NaCl \rightarrow 2NaR + \begin{matrix}\text{Ca}\\\text{Mg}\end{matrix}\Big\} Cl_2$$

Calcium and/or magnesium exchanger	Sodium chloride	Sodium cation exchanger	Calcium and/or magnesium chloride
(insoluble)	(soluble)	(insoluble)	(soluble)

The equipment for the process, shown in Fig. 3.2, is a large, closed cylindrical tank in which the zeolite is supported on graded gravel. The water to be softened may flow down through the tank. Auxiliary apparatus includes both brine- and salt-storage tanks. Washing and regeneration may be carried out automatically as well as manually. These softeners are installed in water lines and operated under whatever water pressure is necessary. As the exchanger bed also exerts a filtering action, any sediment from the water or from the salt must be washed off by an *efficient backwash*. This step suspends and hydraulically regrades the resin bed. The water from ion-exchange treatment usually has a hardness level of less than 1 ppm expressed as calcium carbonate. In cases where very hard bicarbonate water is encountered, it is often desirable to treat the water first by the lime process, followed by cation exchange.[8] The lime process actually reduces dissolved solids by *precipitating* calcium carbonate and magnesium hydroxide from the water, whereas the cation resin exchanges

[8]Krisher, Raw Water Treatment in the CPI, *Chem. Eng.* 85 (19) 79 (1978).

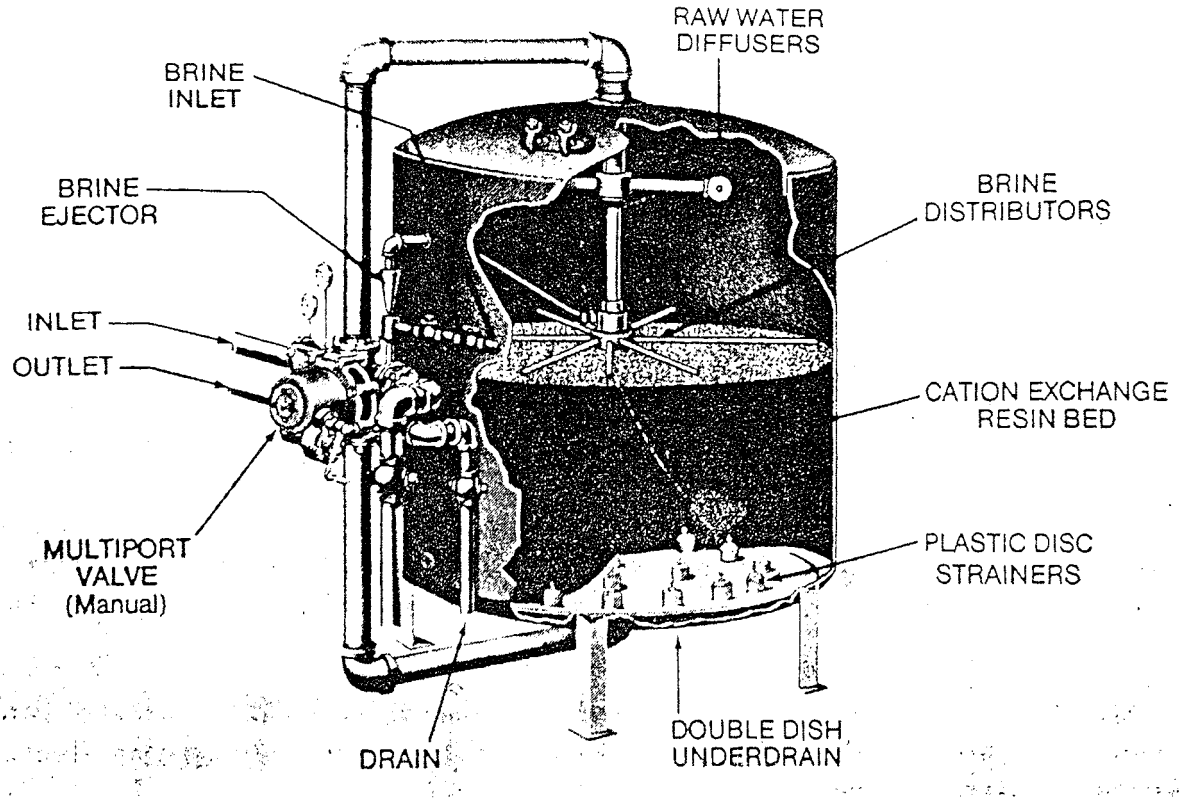


Fig. 3.2. Automatic sodium-cation-exchanger water softener. *(Permutit Co.)*

calcium and magnesium ions for sodium ions. The great advantage of these softeners is their convenience and the fact that they furnish water of very low residual hardness without attention or adjustment until regeneration is required even though the raw water varies in hardness from one day to the next.

The hydrogen-cation-exchange process closely resembles the sodium cation procedure, except that the exchange resins contain an exchangeable *hydrogen ion* and can be employed to remove all cations. The symbol R represents the complex radical for the hydrogen-cation exchanger in the following reactions *for exchanges with bicarbonates*:

$$\left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}(HCO_3)_2 + 2HR \rightarrow \left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}R_2 + 2H_2O + 2CO_2$$

Calcium, magnesium, and/or sodium	Bicarbonate	Hydrogen cation exchanger	Calcium, magnesium, and/or sodium cation exchanger	Water	Carbon dioxide
(soluble)		(insoluble)	(insoluble)		(soluble)

The reactions with *sulfates* and *chlorides*, using the symbol R to represent the organic radical of the exchanger, may be indicated as follows:

$$\left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}\left.\begin{matrix}SO_4\\Cl_2\end{matrix}\right\} + 2HR \rightarrow \left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}R_2 + H_2\left.\begin{matrix}SO_4\\Cl_2\end{matrix}\right\}$$

Calcium, magnesium, and/or sodium	Sulfate and/or chloride	Hydrogen cation exchanger	Calcium, magnesium, and/or sodium cation exchanger	Sulfuric and/or hydrochloric acid
(soluble)		(insoluble)	(insoluble)	(soluble)

Regeneration with sulfuric acid is the most widely used and most economical method of regeneration. The reactions, in condensed form, may be indicated as follows:

$$\left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}R_2 + H_2SO_4 \rightarrow 2HR + \left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}SO_4$$

Calcium, magnesium, and/or sodium cation exchanger (insoluble)	Sulfuric acid (soluble)	Hydrogen cation exchanger (insoluble)	Calcium, magnesium, and/or sodium sulfate (soluble)

Acidic water is not desirable for most purposes, and therefore the effluent from the hydrogen-cation-exchange treatment is either neutralized or blended with sodium zeolite–treated water. If demineralization is required, it is passed through an anion-exchange material, as shown in Fig. 3.3.

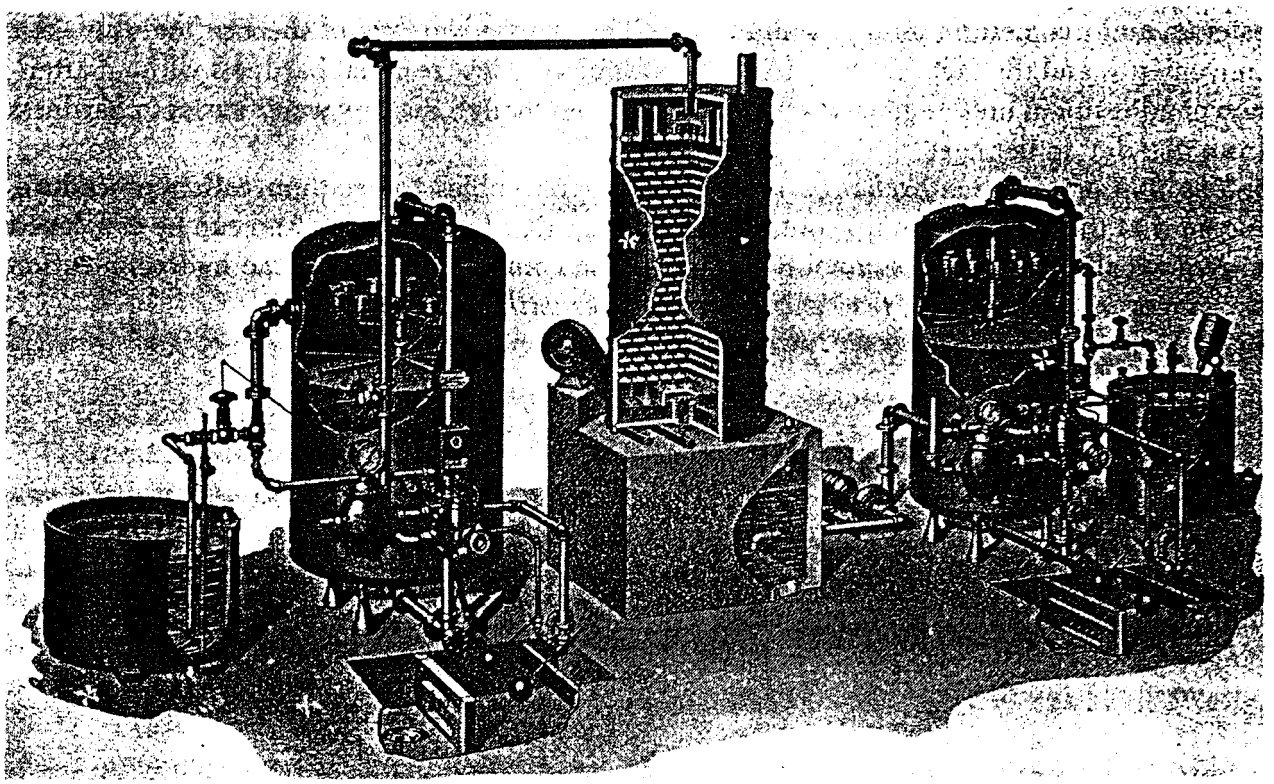


Fig. 3.3. Demineralization equipment in two steps. *(Permutit Co.)*

Anion exchangers are of two resin types, highly basic or weakly basic. Both types will remove strongly ionized acids such as sulfuric, hydrochloric, or nitric, but only highly basic anion exchangers will also remove weakly ionized acids such as silicic and carbonic. For the anion exchange of a strongly ionized acid, where R_4N represents the complex anion-exchanger radical, the reactions follow (some of the R's may be hydrogen):

$$\underset{\text{(soluble)}}{H_2SO_4} + \underset{\text{(insoluble)}}{2R_4NOH} \rightarrow \underset{\text{(insoluble)}}{(R_4N)_2SO_4} + \underset{\text{(soluble)}}{2H_2O}$$

REGENERATION

$$\underset{\text{(insoluble)}}{(R_4N)_2SO_4} + \underset{\text{(soluble)}}{2NaOH} \rightarrow \underset{\text{(insoluble)}}{2R_4NOH} + \underset{\text{(soluble)}}{Na_2SO}$$

Highly basic anion exchangers are regenerated with caustic soda, and weakly basic anion exchangers may be regenerated with caustic soda, soda ash, or sometimes ammonium hydroxide.

Lime-Soda Processes. The use of slaked lime and of soda ash to remove hardness in water has long been important. Modern application has been divided into the cold-lime process and the hot-lime–soda process. The calcium ions in hard water are removed as $CaCO_3$, and the magnesium ions as $Mg(OH)_2$. Typical equations for these reactions are

FOR CARBONATE HARDNESS

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow \underline{2CaCO_3} + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + \underline{CaCO_3} + 2H_2O$$

Then since $MgCO_3$ is fairly soluble, further addition of lime is necessary, causing:

$$MgCO_3 + Ca(OH)_2 \rightarrow \underline{Mg(OH)_2} + \underline{CaCO_3}$$

FOR NONCARBONATE SOLUBLE CALCIUM AND MAGNESIUM SALTS

$$MgCl_2 + Ca(OH)_2 \rightarrow \underline{Mg(OH)_2} + CaCl_2$$

$$CaCl_2 + Na_2CO_3 \rightarrow \underline{CaCO_3} + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \rightarrow \underline{CaCO_3} + Na_2SO_4$$

$$MgSO_4 + Na_2CO_3 + Ca(OH)_2 \rightarrow \underline{Mg(OH)_2} + \underline{CaCO_3} + Na_2SO_4$$

From these reactions it is apparent that, for carbonate hardness, each mole of calcium bicarbonate requires 1 mol of lime, whereas for each mole of magnesium bicarbonate, 2 mol of lime is needed. For noncarbonate hardness, likewise, magnesium salts require more reagent (1 mol each of soda ash and lime) and calcium salts require only 1 mol of soda ash.

The following material quantities have been figures for removing 100 ppm of hardness from 1000 m^3 of water:

Calcium bicarbonate hardness (expressed as $CaCO_3$), 62.4 kg lime.
Magnesium bicarbonate hardness (expressed as $CaCO_3$), 124.7 kg lime.
Calcium noncarbonate hardness (expressed as $CaCO_3$), 103.1 kg soda ash.
Magnesium noncarbonate hardness (expressed as $CaCO_3$), 105.6 kg soda ash, 62.4 kg lime.

The *cold-lime* process is employed chiefly for partial softening and ordinarily uses only cheaper lime for its reagent reactions. It can reduce calcium hardness to 35 ppm if proper opportunity is given for precipitation. This cold-lime process is particularly applicable to the partial softening of municipal water (Figs. 3.4 and 3.5), to the conditioning of cooling water where calcium bicarbonate hardness may be the scale former, and to the processing of certain paper-mill waters where calcium bicarbonate is troublesome. Magnesium carbonate hardness can be removed in any desired economical amount, but, if a low residual is wanted, an excess of hydroxyl ions will be needed to depress the solubility of the magnesium hydroxide. Usually, to aid in the process, a coagulant, aluminum sulfate or ferric sulfate, is added to minimize the carry-over of suspended particles and to a lesser degree to reduce the afterdeposits from the supersaturated effluent. Currently, the use of organic polyelectrolytes is replacing many of the traditional inorganic coagulant aid approaches since the latter can result in carry-over of iron and aluminum which in turn may cause problems downstream.

A successful method of reducing *supersaturation* in the cold-lime–soda process is contacting previously precipitated sludge (Fig. 3.5). When this material is exposed to the raw water and chemicals, the like surfaces, or "seeds," accelerate the precipitation. The result is a more rapid and more complete reaction with larger and more easily settled particles in the newly formed precipitate. The equipment developed for this contact, by Infilco, Inc., is called the Accelerator. The Permutit Spaulding Precipitator[9] consists of two compartments, one for mixing and agitating the raw water with the softening chemicals and with the previously formed sludge, and the other for settling and filtering the softened water as it passes upward through the suspended blanket of sludge. Machines of these types reduce sedimentation time from 4 h to less than 1 h and usually effect savings in chemicals employed.

[9]Nordell, *Water Treatment for Industrial and Other Uses*, 2d ed., Reinhold, New York, 1961 p. 495.

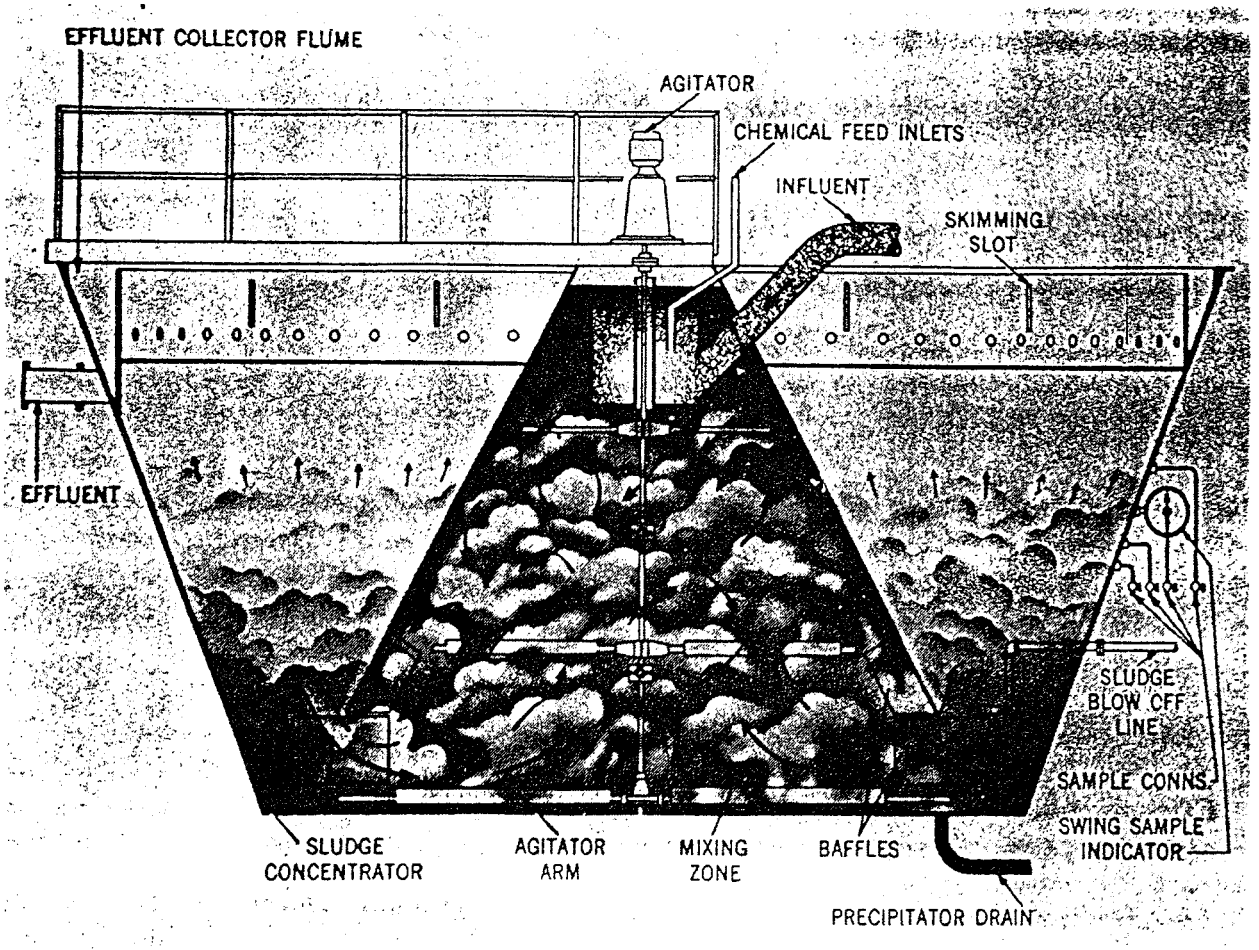


Fig. 3.4. Drawing of precipitator, showing formation of precipitate and upward filtration through sludge blanket. *(Permutit Co.)*

The most objectionable feature of the cold-lime–soda process is the voluminous wet sludge that is formed. Disposal of this sludge has proved to be both troublesome and expensive. The Permutit Spiractor utilizes catalytic precipitation; this reduces the volume and water content of the residual sludge so that the resulting volume is about 12 percent of that of conventional processes, and the resultant waste is similar to wet sand.

The *hot-lime–soda process* is employed almost entirely for conditioning boiler feedwater. Since it operates at the boiling point of the water, the reactions proceed faster, coagulation and the precipitation are facilitated, and all of the dissolved gases, such as carbon dioxide and

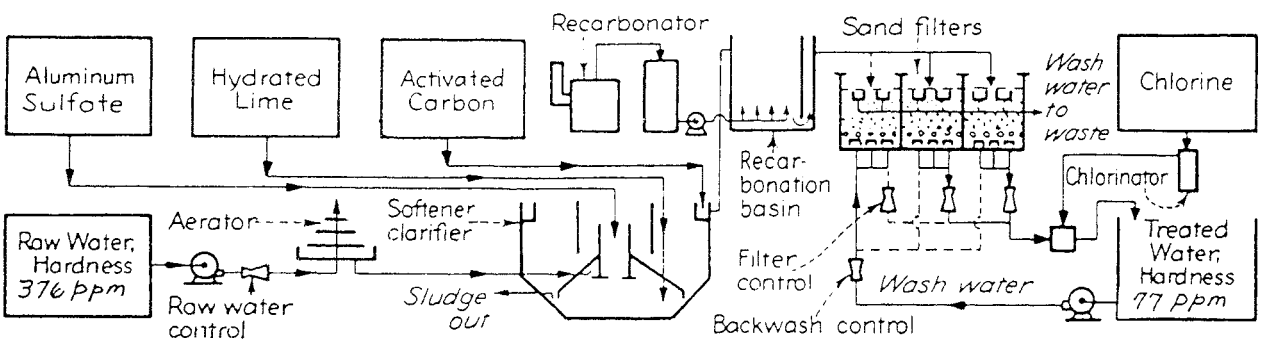


Fig. 3.5. Municipal water-treatment flowchart. *(Infilco, Inc.)*

air are driven out. The hot-lime–soda treatment for softening may consist of the following coordinated sequences, as illustrated by Fig. 3.6:

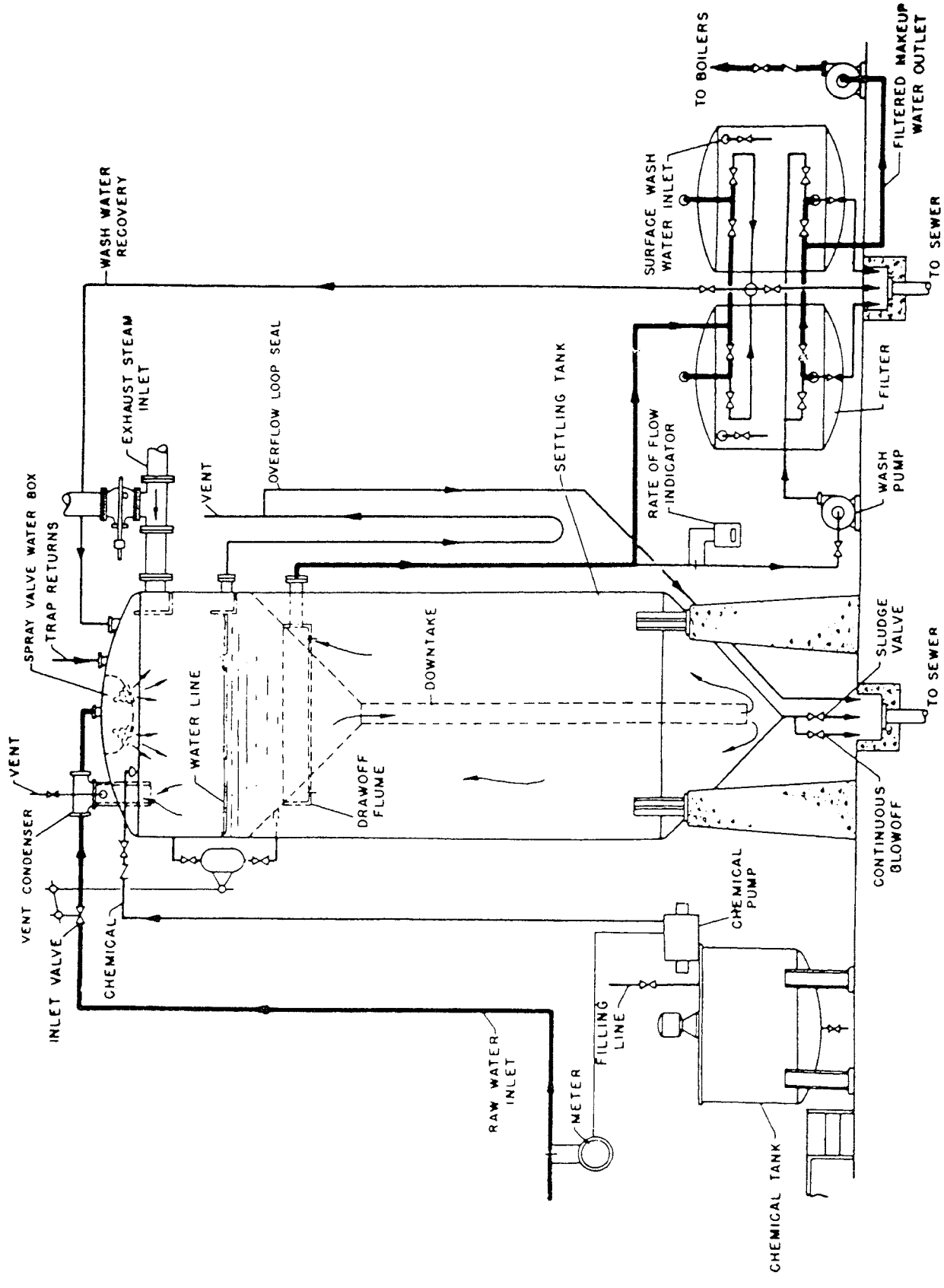
Analysis of the raw water
Heating of the raw water by exhaust steam
Mixing and proportioning of the lime and soda ash in conformance with the raw-water analysis
Pumping of the lime slurry and soda
Reaction of the lime and soda, facilitated by mixing with or without previous heating
Coagulation or release of the "supersaturation" by various methods, such as slow agitation or contact with "seeds" by sludge recirculation
Settling or removal of the precipitate with or without filtration
Pumping away of the softened water
Periodic washing away of the sludge from the cone tank bottom (and from the clarifying filters)

If the chemical reactions involved could be carried to completion, the hardness of the water would be reduced to the theoretical solubilities of the calcium carbonate and magnesium hydroxide. This would leave a hardness of approximately 20 to 25 ppm in pure water, and a little less at the pH 10 to 11 involved in the lime-soda process. The newest development is the use of resinous ion exchangers for more complete softening of the effluent of a hot-lime process. This is particularly necessary when feeding high-pressure boilers.

Phosphate Conditioning. Various phosphates are employed, usually in conjunction with one of the previously described procedures. This process is used in internal conditioning of boiler water, on the one hand, and conditioning of cooling and process water, on the other. Orthophosphates, such as trisodium phosphate, and complex phosphates, such as sodium hexametaphosphate, are both used in steam boilers to precipitate whatever small amounts of calcium ion reach the boiler water through the pretreatment system or by leakage through the condenser. Sodium hexametaphosphate is advantageous where the boiler water naturally tends to become too alkaline, because it reduces this excess alkalinity by reverting to an acid orthophosphate in the boiler. Threshold treatment of cooling and process water with few parts per million of sodium hexametaphosphate depends on other properties of this complex phosphate. When added to water which would normally deposit calcium carbonate scale when made more alkaline or when heated, it inhibits precipitation. Sodium hexametaphosphate is also widely used for minimizing the corrosion and pickup of iron by water in circulating cooling systems, in plant water distribution systems, and in municipal systems.[16]

Silica Removal. Silica is not removed by hydrogen-cation exchange or sodium zeolite exchange and usually is only partially removed in cold- or hot-lime–soda processes. It may be a very objectionable impurity, since it can form a tenacious scale. Silica may be removed from feedwater by the use of dolomitic lime or activated magnesia in the softener. If preliminary coagulation and settling are carried out, the use of a ferric coagulate will remove some silica. These are especially suitable when the silica concentration of makeup water is high.

[16]Illig, Glassy Phosphate in Water Treatment, *J. Am. Water Works Assoc.* **49** 505–516 (1957); Bellow, Comparing Chemical Precipitation Methods for Water Treatment, *Chem. Eng.* **85** (5) 85 (1978); see Chap. 16, Phosphorus Industries.


TO BOILERS
FILTERED MAKEUP WATER OUTLET
SURFACE WASH WATER INLET
TO SEWER
WASH WATER RECOVERY
EXHAUST STEAM INLET
OVERFLOW LOOP SEAL
SETTLING TANK
FILTER
RATE OF FLOW INDICATOR
WASH PUMP
VENT
SPRAY VALVE WATER BOX
TRAP RETURNS
DOWNTAKE
SLUDGE VALVE
TO SEWER
WATER LINE
VENT
DRAWOFF FLUME
CONTINUOUS BLOWOFF
VENT CONDENSER
CHEMICAL PUMP
INLET VALVE
CHEMICAL
RAW WATER INLET
METER
FILLING LINE
CHEMICAL TANK

Such methods do not entirely remove the dissolved silica, but they do lower its concentration to a point where adequate blowdown will eliminate the danger of scale in a boiler. The most commonly used method of producing water with only a trace of silica is demineralization.

Deaeration. Deaeration of water is often necessary to condition water properly for industrial boiler use, although this is unnecessary for municipal waters. Dissolved oxygen hastens corrosion by a number of reactions[11] depending on conditions. The following is a typical outline of an important phase of iron water corrosion accelerated by oxygen under alkaline or neutral conditions. Iron in contact with water exerts a certain solution pressure and sets up the anodic half reaction:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e$$

This ceases after a certain potential is reached. However, oxygen can react with water to give OH ions at the cathode:

$$O_2(g) + 2H_2O(l) + 4e \rightarrow 4OH^-(aq)$$

The Fe^{2+} and the OH^- ions react, and the electrons are neutralized by the flow of current between the adjacent anode and cathode:

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$$

The initial reactions then proceed further. This electrochemical corrosion can be summarized:

$$2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe(OH)_2(s)$$

Naturally, air and water can change ferrous hydroxide to ferric hydroxide. Anything that stops the foregoing sequences will stop the corrosion. This may be accomplished by removal of the dissolved oxygen, by electrode polarization, by organic inhibitors, or by protective salts. Such protective salts are chromates, silicates, phosphates, and alkalies, which probably act as anodic inhibitors by forming a film over the anodic or active areas and thus interrupt the electrochemical sequence. Water ordinarily saturated with air at 10°C contains about 8 ml of oxygen per liter. In preparing boiler feedwater, oxygen is removed by spraying or cascading the water down over a series of trays contained in a pressurized vessel. During the downward flow, the water is scrubbed by steam rising upward. Closed deaerating heaters of this type, operating at approximately 105°C, will generally lower the dissolved oxygen content

[11]For corrosion of metals in contact with liquids, see Nordell, op. cit. pp. 100ff.

To produce 1000 m^3/day of 77 ppm water requires:

Raw water (376 ppm)	1018 m^3	Chlorine	0.82 kg
Hydrated lime	353 kg	Electricity	98 MJ
Aluminum sulfate	18 kg	Direct labor	8.7 work-h
Activated carbon	0.82 kg		

Fig. 3.6. Hot-lime–soda water softener. *(Permutit Co.)*

to below 10^{-2} ppm. Any remaining traces of oxygen can then be chemically combined by using an oxygen scavenger such as sodium sulfite or hydrazine hydrate.

$$O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4$$
$$O_2 + N_2H_4 \cdot H_2O \rightarrow 3H_2O + N_2$$

Such complete deoxygenation is desirable to minimize corrosion in the modern high-temperature high-pressure boiler.

Demineralization and Desalting. Demineralization systems are very widely employed, not only for conditioning water for high-pressure boilers, but also for conditioning various process and rinse waters. The ion-exchange systems chosen vary according to (1) the volumes and compositions of the raw waters, (2) the effluent-quality requirements for different uses, and (3) the comparative capital and operating costs. Briefly, if silica removal is not required, the system may consist of a hydrogen-cation-exchanger unit and a weakly basic anion-exchanger unit, usually followed by a degasifier to remove, by aeration, most of the carbon dioxide formed from the bicarbonates in the first step. When silica removal is required, the system may consist of a hydrogen-cation-exchanger unit and a strongly basic anion-exchanger unit, usually with a degasifier between the units, as shown in Fig. 3.3, to remove carbon dioxide ahead of the strongly basic anion-exchanger unit. For uses where the very highest quality of effluent is required, this may be followed by secondary "polishing" unit(s) consisting of either (1) a hydrogen-cation-exchanger unit and a strongly basic anion-exchanger unit or (2) a single unit containing an intimately mixed bed of a hydrogen-cation exchanger and a strongly basic anion exchanger.

The only other process for removing all the ions in water is *distillation*. Both distilled water and deionized water should be transported through stainless steel or glass to keep the pure water from corroding the transport lines. Block tin has been employed for this purpose for many years but has the disadvantage of extreme softness. Aluminum and molded polyvinyl chloride pipes are now reasonably satisfactory substitutes for conducting "pure" water. Polyethylene, polypropylene, and polycarbonates are also sometimes used.

Desalting, or desalinization, is commonly applied to any process used to effect (1) partial or (2) complete demineralization of highly saline waters such as seawater (35,000 ppm of dissolved salts) or brackish waters. Process 1 applies to lowering the saline content to a degree which renders the water suitable for drinking purposes (preferably 500 ppm salines or less) and other general uses. Process 2 applies mainly to furnishing water suitable for use in high-pressure boilers and for certain other industrial uses. The ion-exchange demineralization processes described earlier in this chapter are not applicable to the desalting of highly saline waters; so other processes must be used.

The main methods in current practice in the United States are electrodialysis and reverse osmosis. Several other methods have been used including multistage flash evaporation, vertical tube evaporation, vapor compression, and vacuum-freeze vapor compression. The high cost of heat has contributed to the ongoing switch from thermal plants to reverse osmosis ones. Worldwide, however, thermal plants comprise 80 percent of the total.[12]

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[12]Water Desalination Gets Another Look, *Chem. Eng. News* 58 (5) 26 (1980); Desalting Takes Off, *Chem. Eng.* 85 (6) 41 (1978); Barduhn, The Status of Freeze-Desalination, *Chem. Eng. Prog.* 71 (11) 80 (1975); Wagner and Finnegan, Select a Seawater-Desalting Process, *Chem. Eng.* 90 (3) 71 (1983)

The usual cost of reverse osmosis desalting is 20 to 30 percent lower than desalting by the thermal units. The makers of the various thermal processes are busy trying to improve their economic considerations. One of the newest processes combines vertical tube evaporation and vapor compression and increases the performance ratio (PR) from 21 to 42.[13] The performance ratio is the kilograms of product per kilogram of heating steam, or in the case of a reverse osmosis process, an equivalent performance ratio. The usual multistage flash evaporation process has a PR maximum of 14 and reverse osmosis has 24.

Many Middle Eastern countries are very actively engaged in installing desalting equipment. The U.S. Office of Water Research and Technology has estimated that the total installed capacity there was 2×10^6 m^3/day in 1978 and will be 20×10^6 m^3/day by the year 2000. All types of processes are currently in use, but the new plants being built are nearly all reverse osmosis units.

The largest desalting plant in the world is being built near Yuma, Ariz., in response to the treaty between the United States and Mexico that requires that the salt content of the Colorado River as it enters Mexico be no more than 115 mg/L (ppm) over the average salinity of the water above the Imperial Dam farther upstream. The treaty also specifies that the United States will deliver to Mexico 17.3×10^8 m^3 of water per year. The Colorado River at the Imperial Dam is used to irrigate Arizona's Gila River Valley, and when this water drains back to the river it may contain as much as 3200 ppm total dissolved solids. This incoming water raises the salinity of the river to as much as 1500 ppm, making the water unusable for agricultural use.

This desalting plant will be a reverse osmosis unit and is designed for a capacity of 360,000 m^3/day of water having a dissolved solids content of no greater than 283 ppm. This water will be blended with raw water to add an additional 14.8×10^6 m^3/year to the Colorado River as it enters Mexico and thus allow the United States to meet its treaty obligations.

Electrodialysis (ED) utilizes ion-exchange membranes in an electric field and depends upon the fact that, when a direct electric current is passed through saline water in a series of closely spaced, alternately placed, cation-exchanger and anion-exchanger membranes, cations pass through the cation-exchanger membranes and anions through the anion-exchanger membranes, resulting in a salinity decrease in one space and a salinity increase in the next space, and so on throughout the stack (Fig. 3.7). The water of increased salinity may be run to waste, and the water of decreased salinity may be recirculated through the stack or passed through a series of stacks. This process does not produce completely demineralized water but reduces the salinity of brackish water so as to make it suitable for drinking and general uses. The ion removal may vary between 20 to 60 percent per stack. A new refinement of this process reverses the polarity of the electrodes periodically and simultaneously the product and waste streams are interchanged. According to the designers, this system prevents the formation of calcium carbonate and calcium sulfate scale. A large installation is on the island of Corfu, Greece, and a plant for Wrightsville Beach, N.C., is being constructed.

Reverse osmosis (RO) utilizes the application of pressure above the osmotic pressure to force pure water through a semipermeable membrane from the concentrated brine solution. This is the opposite of the ordinary osmosis process in which water flows through a membrane from the solution of lower concentration to the one of higher concentration. RO has become feasible because of the development of special membranes. These are of two types: bundles

[13]Channabasappa, Status of Reverse Osmosis Desalination Technology, *Desalination* 17 31 (1975); Why Is Rotunda Still an RO Success? *Water Wastes Eng.* 17 (7) 24 (1980); Hughes and Emmermann, VTE/VC for Sea Water, *Chem. Eng. Prog.* 77 (7) 72 (1981).

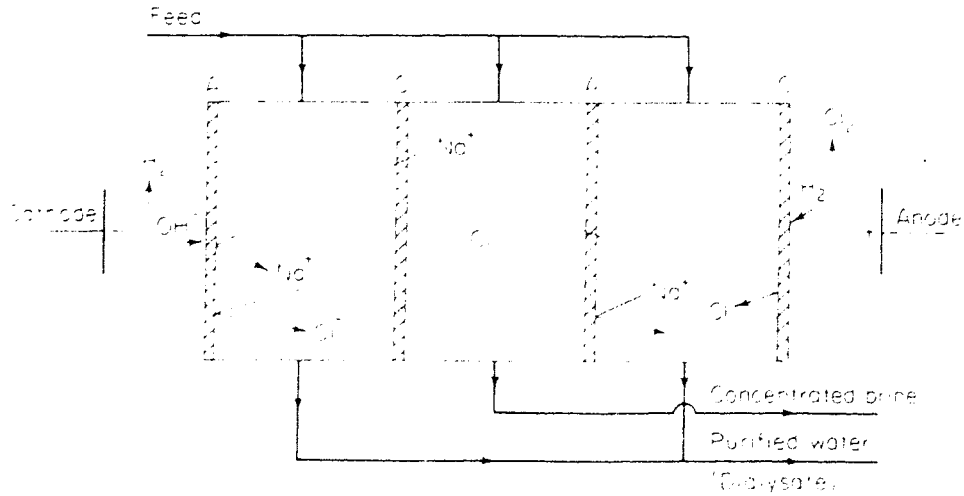


Fig. 3.7. Electrodialysis system for decreasing the salinity of water

of very fine capillaries and spiral-wound sheets. The membrane material may be cellulose acetate (preferred for brackish water) or polyamides (preferred for seawater).

Purification. Treatment of municipal water supplies is usually necessary to produce potable and safe water.[14] Prior to widespread municipal water treatment, epidemics, particularly of typhoid fever, were caused by contaminated water. The requisites of a safe municipal water supply are freedom from pathogenic microorganisms and from suspended solids. It is also desirable, but not necessary, that the water be soft and not have an objectionable taste or odor.

Coagulation and filtration through sand or hard coal and oxidation by aeration are usually sufficient to remove organic matter. This treatment also removes some of the microorganisms. As a further decrease is usually considered necessary in order to produce safe or potable water, treatment with chlorine is indicated. Large quantities of this compound are consumed in this manner to protect the health of the nation. Chloramine, ozone, and chlorine dioxide are also employed. Chloramine is made by feeding ammonia into the chlorinated water.

$$2NH_3 + Cl_2 \rightarrow NH_2Cl + NH_4Cl$$

This produces a better-tasting water in certain instances, but chloramine is a poorer disinfecting compound than chlorine.

Figure 3.5 shows a flowchart for a municipal water-treating plant in which both purification and softening are carried out. The raw water is aerated to remove iron, odor, and taste, partly softened with lime, and the precipitate coagulated and filtered. Chlorine may be added to destroy pathogenic microorganisms, and activated carbon may be employed to remove odors and to improve flavor.

Modern analytical techniques now allow the detection of minute quantities of organic contaminants never before suspected. These appear as mutagenic chlorinated organic compounds, and the amounts may be reduced by chlorinating the water after filtration or coagulation and settling, which is when the organic content is lowest. Activated carbon and resin

[14]Water Treatment Activates Carbon Expansion, *Chem. Week* **127** (8) 32 (1980); Steel and McGhee, *Water Supply and Sewerage*, McGraw-Hill, New York, 1979; Legan, Ultraviolet Light Takes on CPI Role, *Chem. Eng.* 89 (2) 95 (1982); Miller, Your Drinking Water, *CHEMTECH* **12** (8) 456 (1982).

are useful in removing organic compounds, and ozone, chlorine dioxide, or chloramine can be used instead of chlorine to kill the pathogenic organisms and decrease the amount of organic compounds that will be chlorinated. Another method of reducing mutagen levels is by dechlorinating with sulfites and then rechlorinating the water with chloramine.

More than 1300 municipalities have adopted softening as part of their water treatment, but the public as yet does not realize the economic advantages of this process. The savings in soap alone are often more than sufficient to pay for the cost, though these savings have been greatly reduced by the replacement of soap by synthetic detergents for washing purposes. The many other advantages of soft water are therefore essentially free to the user.

ENVIRONMENTAL PROTECTION

The protection of the environment is requiring more attention from chemical engineers every year. Environmental factors affect almost every sector of the chemical process industries as well as industry and business in general. Expenditures for pollution control for 1981 and those planned for 1982 to 1985 are shown in Table 3.2.

The current large expenditures for pollution control in the United States reflect mainly the intervention of the federal government with strict laws. These laws are enforced by the Environmental Protection Agency (EPA). Federal water pollution laws were enacted in 1948, 1956, 1961, 1965, 1966, and 1970, but they were primarily involved in aiding states in establishing limitations for interstate waters. The nation's initial program covering all navigable waterways was passed in 1972 and is known as the *Water Pollution Control Act of 1972*. This law established effluent guidelines for both private industry and municipal sewage treatment plants on a national level. In addition, the law set the ambitious goal of prohibiting the discharge of any type of pollutant into U.S. waters by 1985. A focal point of the 1972 law is the *National Pollutant Discharge Elimination System* (NPDES), which regulates point sources of water pollution. The law states that a NPDES permit is required for the discharge of any type of pollutant. A permit does not condone pollution but rather controls the type and amount of effluent from each source. Target dates for reducing the amount of discharge in accordance with a goal of zero discharge are arranged with the recipient of the permit, who is legally bound to obey the conditions under threat of a possible stiff penalty.

Federal legislation on air pollution control in the United States followed a pattern somewhat similar to that enacted for water. It was 1955 before the first federal law was enacted as the *1955 Air Pollution Act*. This provided for research on air pollution effects by the Public Health Service, some technical assistance to the states, and the training of personnel in the area of air pollution control. In 1963 the *Clean Air Act* provided federal financial assistance but left the control problem to the states. The *1965 Amended Clean Air Act* established the first federal emission standards for cars. The *1967 Air Quality Act* covered the first requirement for ambient air standards, but these were to be set by the states. Finally, in 1970, the 1967 act was amended into strong legislation, which has become known as the *Clean Air Act*. This act provided for:

1. Additional research efforts and funds
2. Additional state and regional grant programs
3. National ambient air quality standards to be set by the federal government
4. Complete designation of air quality control regions

Table 3.2 CPI Pollution Control Expenditures (millions of dollars)

Industry	1982, Planned			% Change, 1981–82			Planned 1983–85 Annual Average		
	Air	Water	Solid Waste	Air	Water	Solid Waste	Air	Water	Solid Waste
Chemicals	510	622	183	112.5	31.5	−2.1	575	701	200
Pulp and paper	228	193	19	24.6	36.9	375.0	311	250	28
Rubber	33	61	33	26.9	125.9	230.6	41	78	41
Petroleum	607	660	63	−7.0	2.5	8.6	541	938	62
Nonferrous metals	126	75	51	5.9	2.7	21.4	176	101	70
Stone, clay, and glass	59	51	6	−35.9	−7.3	−40.0	80	52	6
Total CPI	1563	1662	355	19.0	17.6	14.1	1724	2118	407
Total manufacturing	2416	2646	837	7.3	14.3	25.1	2776	3205	980
All U.S. business	4828	4093	1616	1.3	15.5	28.5	4978	4781	1814

SOURCE: *Chem. Eng.* 89 (14) 61 (1982)

5. Implementation plans to meet the standards to be set in item 3 above
6. Standards of performance for new stationary sources to be set by the federal government
7. National emission standards for hazardous air pollutants

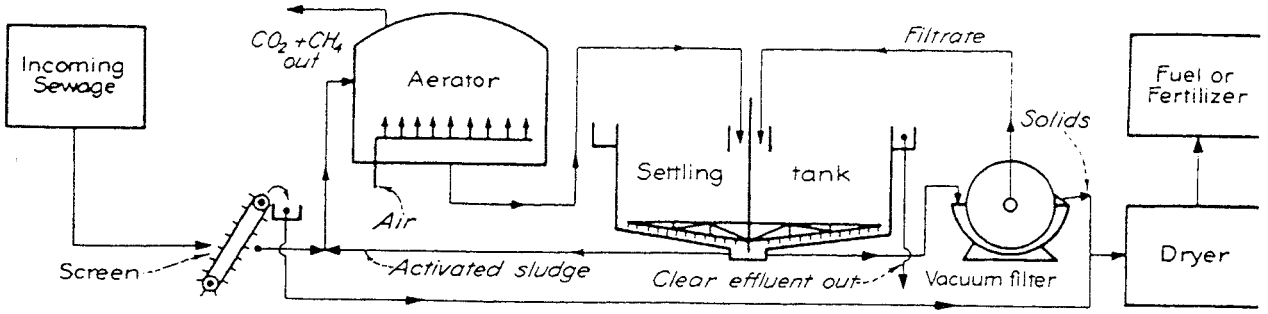
The 1970 act required that industry monitor air pollutants, maintain emission records, and make them available to federal officials. It also covered automobile emission standards, the development of low-emission vehicles, and aircraft emission standards. On December 23, 1971, the first new source performance standards were set by the EPA. These standards covered five types of sources: fossil fuel–fired steam generators (265×10^3 MJ/h input or greater), incinerators, nitric acid plants, sulfuric acid plants, and portland cement plants. Periodically additional such standards are set for other sources. In general the standards are strict and are based on the best pollution control technology available at the time they are set. These are revised frequently. In 1977 additional Clean Air Act Amendments were enacted which further strengthened the role of the government in controlling air quality throughout the United States. There are currently seven air pollutants, called *criteria* pollutants, for which the Environmental Protection Agency has established regulations. The seven are: ozone, carbon monoxide, hydrocarbons, sulfur dioxide, oxides of nitrogen, lead, and particulates.

The 1977 Act requires each state to classify areas that are presently cleaner than the national ambient air quality standard, and allows for a permissible increase in pollution provided that the air will still meet the air quality standard. The goal is to ensure that the air in clean air areas does not significantly deteriorate but still to allow some industrial growth.

MUNICIPAL WASTE WATERS. Efficient *sewage disposal* is important to the health of any community. The easy method of disposal in the past was by dilution; the waste was dumped into an available body of water such as a river or lake, where the already present oxygen would in time destroy the organic sewage. However, dilution is no longer tolerated even in places where it is satisfactory.[15] There is simply not enough water with which to dilute the large amount of wastes from our increasing population and industry. Soon pollution controls will also restrict the dumping of sewage into the sea or the barging out to sea of sewage solids, which become much more concentrated in sewage treatment plants. The federal Water Pollution Control Act Amendments of 1972 require that by 1983 the best practicable waste treatment technology be used and that by 1985 the goal of zero discharge will be met.

The impurity in a particular sewage or, in other words, the amount of treatment required, is usually measured on one of two bases: (1) the amount of suspended solids, which needs no explanation, and (2) the biochemical oxygen demand (BOD), which is the amount of molecular oxygen required by a microbial population to stabilize biodegradable organic material. Present methods of sewage treatment are usually divided into *primary* or physical treatment, *secondary* or biochemical treatment, and *tertiary* treatment. Primary treatment in a simple primary plant is designed to remove from the sewage 30 to 60 percent of the suspended solids and reduce the BOD by a like amount. The effluent is usually chlorinated to destroy bacteria and viruses. In the primary plant the influent is screened to allow the passage of solids not larger than 2.5 to 5 cm. Primary treatment then removes the "settleable" solids. Fine particles may be agglomerated to increase their size and permit settling, so that *coagulation* of fine particles makes larger ones by *flocculation*, and these are then removed by *sedimentation*. The total process is a *clarification* operation. (See Fig. 3.8.) Coagulants are added to assist in

[15]Othmer, The Water Pollution Control Act: Reaching toward Zero Discharge, *Mech. Eng.* 96 (9) 32 (1973); Chronology for Clean Water, *Chem. Week* 130 (13) 28 (1982).



Average technical data:

Air required	2.6 to 14.3 m^3 per cubic meter of sewage
Detention in aeration tank	4 to 6 h
Detention in settling tank	1½ to 2 h
Sludge return to aerator	10 to 50 percent of total

Fig. 3.8. Activated-sludge sewage disposal.

these operations. The chemical additives include inorganic salts, usually of iron or aluminum (ferric sulfate or aluminum sulfate with lime) which, under alkaline conditions, form hydrated colloidal flocs of their hydroxides. Polyelectrolytes (organic polymers) are also used.

Primary treatment alone is now considered inadequate, since it leaves much of the fine particles as well as all of the material in solution. With secondary treatment, dissolved organic materials are oxidized to reduce the BOD by 85 to 90 percent. This imitates nature's conversion by animal microorganisms which feed on them. Gases are formed, and a much smaller mass of solids remains. Biochemical oxidation may be accelerated in the secondary treatment by a trickling filter or an activated-sludge system, as shown in Fig. 3.8. *Activated sludge* provides one of the most effective methods for removing both suspended and dissolved substances from sewage. Activated sludge contains aerobic microorganisms that digest raw sewage. Some activated sludge from the previous run is introduced into the raw sewage, and air is blown in, not in excess but only in the amount needed. Disposal of the solids removed by any of these processes depends upon local conditions. In some cases they are buried, burned, or sold as fertilizer after filtering and drying. The liquids remaining after the removal of the solids are usually chlorinated to destroy harmful microorganisms and then discharged into nearby streams.

In recent years, oxygen-producing companies have developed processes using oxygen rather than air to speed up the aerobic treatment of sewage.[16] Union Carbide with its UNOX System is active in this field. This is a multistage operation utilizing the highest purity oxygen in the first stage where the requirements of the sludge being treated are highest. The oxygen is dissolved using low-speed surface aerators or, in large installations, with a submerged spurge turbine. Figure 3.9 shows a typical UNOX system.

Another system of oxygenation of sewage is the PROST system,[17] which utilizes pressure digestion with air and/or oxygen. The influent sewage liquid is mixed with air, oxygen, or a mixture of the two in a centrifugal pump and passed to a pressure vessel at pressures of 200 to 500 kPa. As the oxygen is dissolved rapidly in the pump, it is almost completely dissolved

[16]Fallwell, Oxygen Finding a Big Outlet in Treatment of Wastewater, *Chem. Eng. News* 52 (28) 7 (1974); Gross, The UNOX Process, *Chem. Eng. Prog.* 72 (10) 51 (1976).

[17]Othmer, Oxygenation of Aqueous Wastes, *Chem. Eng.* 84 (13) 117 (1977).

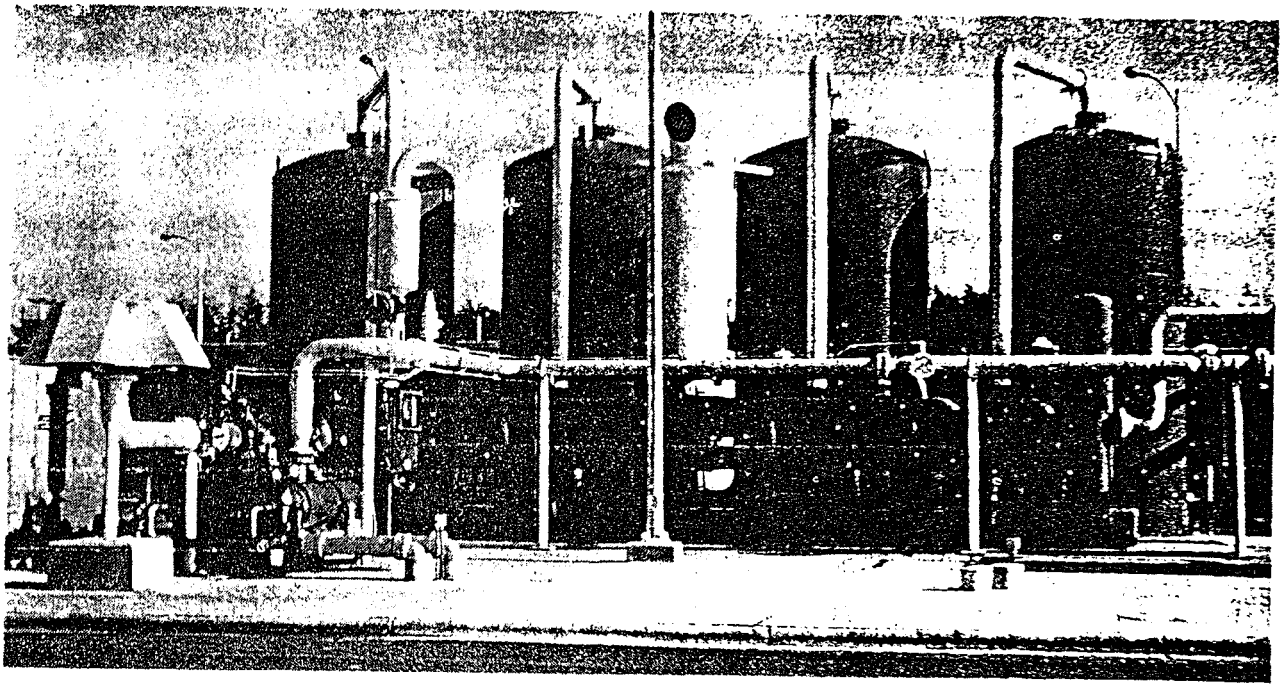


Fig. 3.9. UNOX system at Morgantown, N.C. The system is supplied oxygen by a 25.5-t/day pressure-swing adsorption (PSA) oxygen plant.

by the time the mix reaches the pressurized digestor, and oxidation takes place so calmly that the digestor may be simultaneously used as a clarifier to settle out the sludge. The liquid then overflows the top with a BOD reduction of 80 to 90 percent and a near absence of turbidity.

High-purity oxygen enjoys a basic economic advantage over air because of energy considerations. The volume of oxygen dissolved per unit of electrical power consumed is at least 4 times that of oxygen in air, but the amount of energy needed to separate oxygen from air is relatively low. Oxygenation systems have other cost advantages, e.g., with regard to treatment capacity. With oxygen systems, the size of the plant may be reduced from one-half to one-third the size of one operating on air. Also, there is a lower rate of sludge generation, and the new systems can adjust quickly to sudden overloads of waste, a frequent problem in secondary treatment plants. Another side benefit is that odors are virtually eliminated because covered aeration tanks are used. Table 3.3 shows a comparison of air versus oxygen for secondary treatment.

A new development for secondary treatment is the use of fluidized beds, which combine the best features of trickling filters and activated sludge systems.[15] This system consists of a bioreactor partially filled with sand. Wastewater passing upward through the bottom of the reactor imparts motion to the sand and "fluidizes" it. This expanded sand presents a vast surface to support a biological population. The surface of the sand eventually becomes covered with a firmly attached biomass which then consumes the waste materials in the wastewater. The concentration of the biomass is an order of magnitude greater than conventional activated sludge systems. Thus, the bioreactor's volume may be as little as 10 percent of that of the conventional reactor.

When compared with the usual aerobic process, anaerobic fermentation is an energy-saving, biological method of removing organic matter from wastewater. This process has the

[18]Barbara, Flood, and Jeris, Fluidized Beds Improve Treatment, Cut Costs, *Water Wastes Eng.* **17** (6) 35 (1980); Space Saving Wastewater Treatment, *Chem. Eng.* **86** (14) 47 (1979).

Table 3.3 Sewage Treatment with Oxygen versus Air

	UNOX System	Conventional Air System
Mixed liquor dissolved oxygen level, mg/L	4–8	1–2
Aeration detention time (raw flow only), h	1–3	3–8
MLSS* concentration, mg/L	4500–8000	1000–3000
MLVSS† concentration, mg/L	3500–6000	900–2600
Volumetric organic loading, kg BOD/(day)(100 m^3)	240–400	50–100
Food/biomass ratio BOD/MLVSS, w/w	0.4–1.0	0.2–0.6
Recycle sludge ratio, recycle/feed, w/w	0.2–0.5	0.3–1.0
Recycle sludge conc., mg/L	15,000–35,000	5,000–15,000
Sludge volume index (Mohlman)	30–70	100–150
Sludge production, VSS/BOD removed, w/w	0.4–0.55	0.5–0.75

*Mixed liquor suspended solids.

†Mixed liquor volatile suspended solids.

SOURCE: Linde Division, Union Carbide Corp.

advantage of being able to treat wastewater high in organic material (>1000 mg/L BOD) and to convert over 90 percent of the biodegradable material into methane.[19]

A combination of primary and secondary treatments of municipal wastewater into one process utilizes a novel approach. The water hyacinth, long regarded as a weed, appears to thrive on sewage. It floats on the surface, and its roots adsorb the waste materials including toxic materials and heavy metals.[20] The process is efficient and economical.

Tertiary sewage treatment involves further processing steps after secondary treatment, usually for the removal of pollutants with no BOD. After secondary treatment, water still contains phosphorus, nitrogen, and carbon compounds in solution, which can serve as nutrients for the overabundant growth of algae and other aquatic plants. The enrichment of waters with nutrients is referred to as *eutrophication* (derived from the Greek words *eu*, meaning "well," and *trophein*, "to nourish"). Since phosphorus, a major ingredient required for growth, is used in detergents (see Polyphosphates, Chap. 16), excess growth of algae in natural waters receiving domestic waste discharges is generally blamed on the high phosphorus content of the water. Since complete removal of phosphorus from domestic waste cannot be accomplished by only limiting the use of phosphorus compounds in detergents, considerable work has been done in developing processes for removing phosphates from municipal wastewater. The most common types of chemical treatment are precipitation with lime and/or metallic hydroxides such as aluminum. It is about 90 to 95 percent effective and the cost is less than $1.32 per 100 m^3. Under some conditions, microorganisms can absorb quantities of phosphates greatly in excess of their usual needs, a so-called luxury uptake. This uptake is reversible, as decay of the cells can release the phosphate. A treatment plant, such as the one used in the District of Columbia, has a process that removes the sludge from the final clarifier rapidly and feeds it into a phosphorus stripper operated in the fashion of an anaerobic diges-

[19]Obayashe, Anaerobic Treatment of High-Strength Wastes, *Chem. Eng. Prog.* 77 (4) 68 (1981).

[20]Middlebrooke and Reed, The Flowering of Wastewater Treatment, *Water Eng. Management* 128 (6) 51 (1981); Big Waste Treatment Job for Water Hyacinths, *Chem. Eng.* 88 (9) 34 (1981).

ter. About two-thirds of the phosphate in the sludge is released in the digester and can be removed by chemical means. About 90 percent removal of phosphorus can be accomplished.

In 1980 more than 500 plants in the United States and Canada used chemical treatment methods to remove phosphorus and nitrogen compounds.[21] In 1972 only 10 such plants were operating.

INDUSTRIAL WASTEWATERS. The problem of adequately handling industrial wastewater is more complex and much more difficult than that involving sewage. Increasingly stringent federal, state, and local regulations have been enacted prohibiting or limiting the pollution of streams, lakes, and rivers. The federal Water Pollution Control Act of 1972 set the following goals: July 1, 1977, the utilization of the best practicable control technology currently available; July 1, 1983, utilization of the best available technology economically achievable; July 1, 1985, discharge of pollutants into the nation's water be eliminated. Economic and technical studies are necessary to determine the least expensive way to comply with legal requirements and to reduce expenses or to show a profit through the recovery of salable materials. Other factors, such as reduction in real estate values, danger to inhabitants, and destruction to wildlife, are also involved. The great variety of chemical wastes produced in the nation's factories forces specific treatment in many instances. A few general practices are in use in many fields. One is that of storing, or lagooning, wastes. This may serve many different purposes. In factories having both acid and basic wastes, it reduces the cost of neutralization. In plants having wastewater containing large amounts of organic material (e.g., some paper mills) this results in a decrease in suspended matter and a reduction in the BOD. The use of flocculating agents (alum, $FeSO_4$) to remove suspended solids, and aeration to reduce the BOD, are also common to many industries.

A general problem in all industries is the disposal of wastes obtained as a result of water-softening treatment. Lime sludges may be lagooned and settled, or they may be dewatered and calcined for reuse. This sludge also finds some application in absorbing oil from other wastes. Brine used in regenerating ion-exchange plants is best stored and then added to streams by controlled dilution at high water. When the industry uses raw materials of complicated organic nature, an activated-sludge process may be used to treat the wastes. This process can be adapted to wastes from canneries, meat-packing plants, milk-processing plants, rendering plants, and others.

Many organic compounds are toxic, resistant to natural degradation, and require special handling before they can be safely discharged. One technique for removing these toxic materials from wastewater is by absorption onto activated carbon or a porous polymeric resin. Often the organic material may be removed from the resin with a suitable solvent and recycled. The process has been particularly useful for treating wastewater containing chlorinated pesticides.[22]

Tannery wastes may be treated by flocculation and sedimentation or filtration. Brewery wastes are subjected to trickling filters to reduce the BOD and remove most of the suspended solids. Paper mills have a serious problem, especially in treating sulfite wastes (Chap. 33). The

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[21]Menar and Jenkins, *Environ. Sci. Technol.* 4 1115 (1970); Goldieri, Biological Phosphorus Removal, *Chem. Eng.* 86 (28) 34 (1979); Ockershausen, Chemically Treating Wastewater: An Update, *Water Sewage Works*, Reference No. R-51 (1980).

[22]Fox, Removing Toxic Organics from Waste Water, *Chem. Eng. Prog.* 75 (8) 70 (1979); Holiday and Hardin, Activated Carbon Removes Pesticides from Wastewater, *Chem. Eng.* 88 (6) 88 (1981).

processing of wastes from large chemical plants is exceedingly complex because of the variety of chemicals produced. The Dow Chemical Co. at Midland, Mich., for example, manufactures 400 chemicals in 500 processing plants and laboratories, resulting in a total of 757,000 m^3/day of wastewater. Equalization of acid and basic wastes and other general practices are followed, but many of the wastes are given treatment *at the source*, with an eye to recovery of valuable materials and by-products. Kodak ensures limited pollution of the Genesee River by the use of clariflocculation basins, sludge filtration, and cake disposal and is employing ion exchange to regenerate phosphoric acid used as the electrolyte in anodizing aluminum sheet.

Anaerobic treatment is useful for a wide range of organic wastes and as a bonus, produces methane-rich fuel gas that can be burned in the power plant.[23] Increasing emphasis in industrial-waste treatment is being placed on the recovery of useful materials. Fermentation wastes (slop), after evaporation and drying, are being sold as animal food. The use of ion exchangers promises the recovery of chromium and other metals from plating procedures. Ferrous sulfate (see Recovery of Waste Sulfuric Acid in Chap. 19) is being obtained from pickling operations to a limited extent. The cost of energy is also an important consideration in any method of waste disposal.[24]

In the past the waste streams or sludges containing hazardous chemicals have been injected into deep wells, dumped into the ocean, or stored in a landfill. All of these methods are objectionable for one reason or another, and new regulations are demanding alternative methods of disposal.

Wet air oxidation is one such method and offers an opportunity to recover inorganic chemicals.[25] The oxidation takes place in an aqueous medium at temperatures ranging from 177 to 315°C. Preheated wastewater is reacted with a stoichiometric quantity of compressed air. The exothermic heat of reaction of the organic components with oxygen raises the temperature of the reactor. Temperature and oxidation times can be varied depending upon the waste to be treated.

INDUSTRIAL SOLID WASTES. Most solid wastes are separated as sludge from process or wastewaters and must be treated to render them comparatively harmless before they can be disposed of.[26] *Hazardous* materials range from inorganic salts to organic compounds to radioactive materials. Each type of material may require a different treatment. The sludge is usually dewatered by centrifugation, filtration, and/or heat treatment. Aerobic or anaerobic digestion can remove some organic compounds from organic, petrochemical, and paper processes and thus reduce the BOD of the resultant sludge. However, many inorganic compounds and some organic materials must be chemically fixed. Neutralization of acids or bases is an obvious method. Oxidation of many compounds can convert them into harmless products, but the toxicity of many other compounds cannot be destroyed so readily. Binding into a chemical matrix that is impervious to water penetration is another method of inactivating

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[23]Anaerobic Treatment Cuts Costs, Generates Energy, *Chem. Week* 129 (6) 40 (1981); For License: Anaerobic Wastewater Process, *Chem. Eng. News* 59 (33) 38 (1981).

[24]Fosberg et al., Selecting Energy-Efficient Wastewater Treatment Systems, *Chem. Eng. Prog.* 77 (10) 63 (1981); Prather and Gossom, Designing Wastewater Treatment Systems to Save Energy, *Chem. Eng. Prog.* 77 (10) 68 (1981).

[25]Wilhelmi and Knapp, Wet Air Oxidation, *Chem. Eng. Prog.* 75 (8) 46 (1979); Schaefer, *Hydrocarbon Proces* 60 (10) 100 (1981).

[26]Okey, DiGregorio, and Kominek, Waste-Sludge Treatment in the CPI, *Chem. Eng.* 86 (3) 86 (1979).

hazardous materials. Incineration, both dry and wet, has many variations designed to detoxify waste materials.[27] Pyrolysis[27a] (breakdown without oxidation) appears promising but has not been successful either technically or economically when used to dispose of garbage or tires.

Both *high- and low-level radioactive wastes* have posed difficult disposal problems. Vitrification and granulation are being used to eliminate the need for storing liquid radioactive materials, and thus the possibility of seepage of waste through a deteriorating container. Landfills and storage in deep geologic formations have been the usual method of disposal. However, ecological questions continue to be raised and much research is being conducted into more adequate, safe methods for disposal of this type of waste.[28]

Waste exchanges serve a useful function in finding customers for wastes. They publish listings of wastes available for reuse and of companies seeking particular waste materials, and act as the go-between for both parties. Waste disposal firms are becoming more active in the chemical waste disposal business. They are particularly useful for small companies which do not have the facilities to dispose of their own wastes.[29]

AIR POLLUTION. Air pollution, or atmospheric contamination, is an acute problem throughout the country. Among the many causes of air pollution are industrial operations, transportation vehicles, and incineration of rubbish and waste by individuals. Many contaminants may be eliminated at the point of production, for instance, at the exhaust pipe of an automobile, before smog is formed. For this, catalytic afterburners have been developed. Catalytic exhaust systems were installed on 1975 model cars in the United States to meet the tough emission guidelines of the EPA for hydrocarbons and carbon monoxide. The use of catalytic exhaust systems requires the use of lead-free gasoline, so that the catalyst will not be poisoned by the lead.

Air pollutants leaving chemical processes and other industrial installations may be gases, mists (liquid particles less than 10 μm in diameter), spray particles (liquid particles larger than 10 μm), dusts, fumes, or combinations of these. Electrostatic precipitators are widely used for dust collection, along with baghouses, cyclones, and scrubbers. Mist eliminators have been developed and applied widely in the chemical process industries for the collection of liquid particles.[30]

Of the various gaseous pollutants from industrial processes, sulfur dioxide has probably received the most attention. Sulfur dioxide has been discharged into the atmosphere in large quantities from electric power plants that burn coal and oil containing sulfur. Other sources have included ore-roasting processes for the production of lead, copper, and zinc, and sulfuric

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[27]Evans, Sludge Treatment Process Offers Flexibility, Low Cost, *Chem. Eng.* 84 (26) 86 (1977); Harbold, How to Control Biological Waste-Treatment Processes, *Chem. Eng.* 83 (26) 157 (1976); Waste-Sludge Treatment in the CPI, *Chem. Eng.* 86 (3) 86 (1979).

[27a]Kaplan and Short, Second Chance for Pyrolysis, *Chem. Eng.* 89 (25) 41 (1982).

[28]Pigford, Geological Disposal of Radioactive Waste, *Chem. Eng. Prog.* 78 (3) 18 (1982); *Chem. Eng. Prog.* 72 (3) 43–62 (1976). Contains several articles on handling nuclear waste.

[29]Waste Disposal's Aggressive No. 1, *Chem. Week* 129 (7) 40 (1981); Waste Exchanges Grow in Number and Scope, *Chem. Eng.* 88 (14) 68 (1981); Corbett, Hazardous Waste Managers Are Cleaning Up, *Chem. Mark. Rep.* June 28, 1982, p. 16.

[30]Brink, *Mist Eliminators for Sulfuric Acid Plants, in Sulfur and SO_2 Developments*, Chemical Engineering Progress Technical Manual, AIChE, New York, 1971 pp. 36–40; Brink and Dougald, Particulate Removal from Exhaust Gases, *Pulp Pap.* 47 (1) 51 (1973); see Perry, pp. 18-82 to 18-93 for a complete coverage of mist collection equipment.

acid plants (see Chap. 19). Of these various sources, the electrical power industry problem has been studied the most extensively because of the amount of sulfur dioxide discharged. One approach has been the desulfurization of fuel prior to its use in a boiler. This approach has been used for years by the petroleum industry to produce low-sulfur oil; however, it has not been developed to date for the large-scale desulfurization of coal. A number of stack gas sulfur dioxide removal processes have been worked out for large boilers. The chemical processes under development in the United States include scrubbing with a magnesium oxide slurry, limestone slurry scrubbing, catalytic conversion of sulfur dioxide to sulfur trioxide, spray dryer-type scrubbing in which the slurries are reduced to a dry powder product of the process, dry scrubbing with nahcolite or similar alkaline agents,[31] reaction of SO_2 with sodium sulfite to form sodium bisulfite at relatively low temperatures (Wellman-Lord process), and the absorption of SO_2 by sodium citrate solution (Flakt-Boliden process).[32]

The removal of SO_2 and also NO_x from the flue gases of coal and oil burning is becoming a very important ecological issue.[33] Smokestacks have been built higher and higher to discharge the pollutants high into the atmosphere so that they would not contaminate the surrounding air. However, these noxious gases now are caught by the prevailing winds, changed into nitric and sulfuric acids by contact with moisture in the air, and deposited as "acid rain" perhaps hundreds of miles away from their source. This acid rain may have a pH as low as 1.5, but more often it is about pH 3.5. The effect of this on plant and marine life is disastrous and is certainly not desirable for humans. Forests are rendered quite unhealthy, primarily because of the decrease in soil microorganisms that fix nitrogen. The fish in the lakes that the rain falls upon are becoming stunted or are dying. The cost of reducing sulfur emissions by 3 percent, or by 10^6 t/year,[34] by the electric utilities (which produce 65 percent of the SO_2 emissions) has been estimated at $2000 million in 1981 dollars. To reduce emissions 15 to 30 percent, 6 to 10 $\times$ 10^6 t/year, would cost $5000 to $7000 million. Weighed against these figures the National Academy of Sciences has estimated the cost of the damage in the eastern third of the United States in 1978 to be $5000 million.

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[32]Leckner, Pearson, and Wood, The Wellman-Lord SO_2 Recovery Process, *Chem. Eng. Prog.* 78 (2) 65 (1982); Farrington and Bengtsson, Citrate Solution Absorbs SO_2, *Chem. Eng.* 87 (12) 88 (1980).

[33]*The Debate over Acid Precipitation*, Report by the Comptroller General of the United States, EMD-81-131, Sept. 11, 1981; *Acid Rain Information Book*, U.S. Dept. of Energy, May, 1981; Ember, Acid Pollutants, *Chem. Eng. News* 59 (37) 20 (1981); Baasel, Ball, and Meling, Cost for Control of SO_2 Emissions, *Chem. Eng. Prog.* 78 (6) 47 (1982)

[34]t = 1000 kg.

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Chapter 2

Food and Food By-Product Processing Industries

Much of the technology used in other manufacturing industries has been applied to food. Likewise, much of the technology developed for the food industry is applicable to other industries. The demand for more preprocessing and processing of food products for home use has arisen naturally because many homemakers work away from home. The demand for uniform quality of food on a year-round basis and high quality standards, even at consumption centers remote from production, has led to improved processing methods. Increasing affluence has led to a demand for greater variety.

HISTORICAL. Production and small-scale processing were formerly done on farms and in homes, but with increasing specialization and reduction in the number of people on farms, centralized processing became essential. With central processing, the establishment of grade and quality standards has become necessary. Early developments grew from cottage and community programs (e.g., canneries) into larger-scale units. Milling of grain, fluid milk processing and distribution, baking, and processing of sugar and candy products developed early. More recently, freezing has been applied to meat, fruits, vegetables, and manufactured food products ready to cook or serve. A whole new storage and distribution process had to be developed to permit broad-scale consumption of frozen products. The materials produced on farms, ranches, and plantations, which were formerly consumed or retained there, are now seldom so handled. Production enterprises are now often single-product oriented, buying much of their basic food from manufactured sources. At each step in the movement of the product to the consumer, consideration is given to factors influencing the quality of the product and its value to the ultimate user. However, each step adds to the cost so that the final cost to the consumer is often many times greater than the price paid to the farmer. In 1980[1] total food expenditures in the United States were almost $300,000 million, while the total value of farm marketing was only $125,000 million.

ECONOMICS. The food industry is very large, almost twice the size of the chemical industry. In 1977 processing added $56,000 million in value, approximately thirty percent of the final value of the products. Consumers and producers often accuse the food processing industry of excessive "middle" costs. These costs are, however, similar to the manufacturing costs of other

[1] *The Statistical Abstract of the United States*, 1981

Table 25.1 Size of Some Manufacturing Industries

	Value Produced, 10^9\$	Value Added by Manufacturing, 10^9\$	New Capital Expenditures, 10^9\$	Total Employees, 10^3
All industries	1359	585.2	47.5	13,691
Food	192.9	56.1	4.2	1,509
Chemicals and allied products	118.2	56.7	5.2	54
Petroleum	93.9	16.4	2.6	101
Paper	52	22.2	3.3	486
Textiles	35	16.1	1.2	765
Rubber	38	19.7	1.6	564
Stone, clay, and glass	37	19.1	5.7	484
Leather	8	3.7	0.096	243

SOURCE: *The Statistical Abstract of the United States*, 1981. Data are for 1977.

industries (Table 25.1). Compared with the chemical process industries, the food industry invests and spends less in facilities and equipment and has more employees. This comparison, along with increasing labor costs, suggests a future increase in facilities and equipment investment and a comparative decrease in the number of employees per unit of production. The relative sizes of the various sections of the industry are shown in Table 25.2.

The rising cost of energy has necessitated a revaluation of processes now in use and the development of new processes, as well as exploring energy-saving ideas for current methods of operation.[2] The use of solar energy is being examined and one plant for frying potatoes is in operation.[3] This utilizes solar energy, collected through parabolic trough collectors, to heat pressurized water. This heated water is transformed to steam in a steam-flash-tank and the steam, plus additional steam from a gas-fired boiler, is used to heat the fryer through a heat exchanger. Cogeneration of electricity with process steam is being suggested as a means of conserving energy. It is expected that savings of more than 20 percent can thus be achieved.[4]

[2]Singh, Energy-Saving Ideas for Food Processors, *Food Prod. Manag.* 104 (11) 12 (1982).

[3]Ore-Ida Foods Tests Solar Energy System, *Food Prod. Manag.* 104 (3) 12 (1981).

[4]Outlook For Industrial Cogeneration in Food Processing Plants, *Food Prod. Manag.* 104 (3) 13 (1981).

Table 25.2 Size of Food Manufacturing Industries

	No. Establishments	No. Employees 10^3	Value Added by Manufacturing 10^6\$	Capital Expenditures 10^6\$
Meat products	4,534	254	7,478	535
Dairy products	5,731	154	5,148	382
Fruits and vegetables	2,379	235	7,685	471
Grain mills	3,043	116	6,626	520
Bakery products	3,386	222	7,073	365
Sugar	198	10	1,131	77
Beverages	3,104	195	6,601	344
Fats and oils	80	11	1,405	107
Misc. foods	4,412	146	559	552
All food	26,656	1500	50,526	4215

SOURCE: *The Statistical Abstract of the United States*, 1981. Data are for 1977.

TYPES OF FOOD PROCESSING

REFINING AND MILLING. Sugar is obtained from its plant source (cane or beets) and converted to the common food product by various processes known as *refining*. This is discussed in detail in Chap. 30.

Milling[5] is the process of converting grain into flour by mechanical means. The grain is cleaned and a small amount of water is added to prevent the outer part of the kernel from pulverizing. The moistened grain is crushed slightly between two steel corrugated rolls rotating at high speed and with one roll rotating faster than the other. This exerts a shearing action and breaks the kernel into chunks. The product is sifted to remove the germ and bran, and the chunks are size separated with the larger ones being recrushed and the intermediate-sized ones ground between smooth rolls. The resulting flour is sieved to remove large particles.

The modern milling industry uses many innovations in measuring, metering, weighing, conveying, blending, applying power, sanitation, etc. A new development is the production of free-flowing flour made by agglomerating the flour particles into clusters by the addition of moisture and spray-drying. The use of air classification has made possible the separation of high-protein and high-starch fractions and thus permits a wide range of custom blending.

CANNING. Many types of fresh foods, such as fruit, vegetables, meats, fish, etc., are preserved for long-term storage by heat treatment and sealing into air-tight containers. These containers may be metal, usually tinned or untinned steel, which is often plastic-lined, aluminum, or special-strength glass. The raw food is packed into the container, the container sealed, and the whole package is then heat treated to cook the food and sterilize both the container and the contents. The usual method of heat treating is to place the containers in a steam pressure vessel and process them at 121°C for a time dependent upon the size of the container and the nature of the contents. Acid foods (pH below 4.5) require less time to process than foods with a pH between 4.5 and 7.0. The toxin produced by the microorganism *Clostridium botulinum* is especially toxic to humans, and therefore processing must be severe enough to destroy this organism. It will not grow at a pH lower than 4.5 but it thrives between pH 4.5 and 7.0. Most vegetables, such as beans, peas, and corn, have a pH above 4.5 so that they require more heat treatment than tomatoes, fruits, berries, and pickled products whose pH varies from 2.3 to 4.5.

Heating may degrade the odor and taste of food, and other chemical changes take place during canning. In general, short time–high temperature treatment causes less deterioration than long time–low temperature processes. To ensure adequate heat penetration using a short-time treatment, agitated cookers are often used. Agitation increases the rate of heat transfer from container to product by continuously changing the surface of food in contact with the can.

The agitated cooker consists of a preheater, cooker, and cooler. The cans are placed in individual compartments and rotated by a revolving reel on a spiral track. The track guides the compartments from inlet to outlet continuously. See Fig. 25.1. Other agitated cookers use reciprocating movement of cans held in trays.[6] Rotary pressure sterilizers are used in 26 countries and process 43×10^9 cans annually. A newer system (Fig. 25.2) can process any standard size container.

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[5]Peterson and Johnson, *Encyclopedia of Food Technology*, vol. 2, Avi, Westport, Conn., 1975

[6]Desrosier and Desrosier, *The Technology of Food Preservation*, 4th ed., Avi, Westport, Conn., 1977, chap. 6; *Food Eng.* **54** (7) 138 (1982).

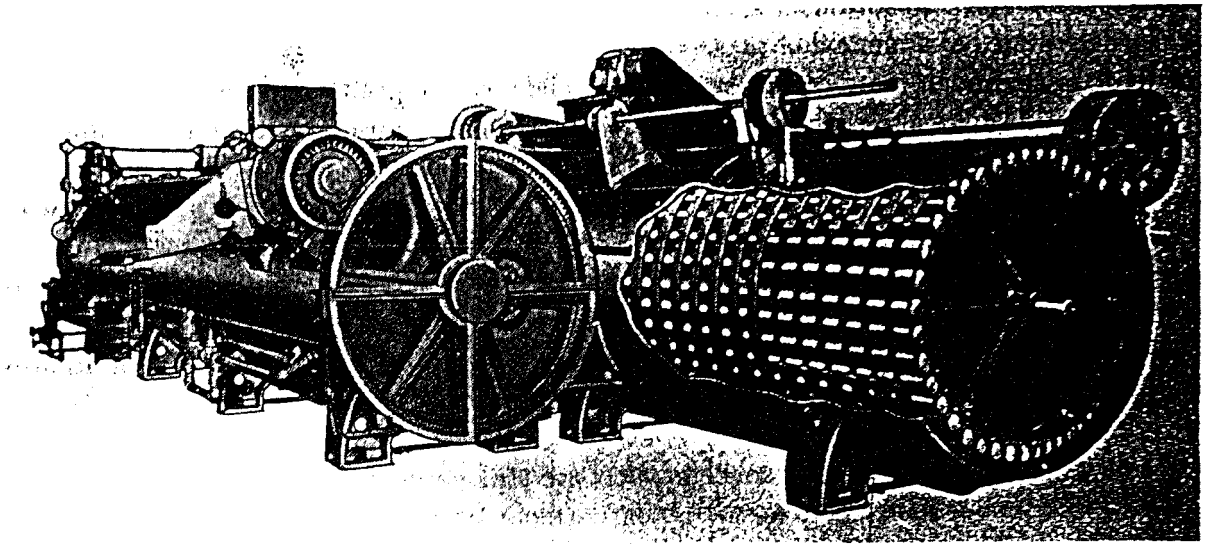


Fig. 25.1. Rotary pressure sterilizer. The shell (tank) on the right is a pressure cooker, and the one on the left is a pressure cooler. Cans enter through a revolving pocket valve, top right, and are carried on a revolving reel. Cans ride against a fixed spiral track which moves them through the shell. The cooler shell, connected by a transfer valve, has a similar reel and spiral system. Cans are discharged through a pocket valve at left. *(FMC Corp.)*

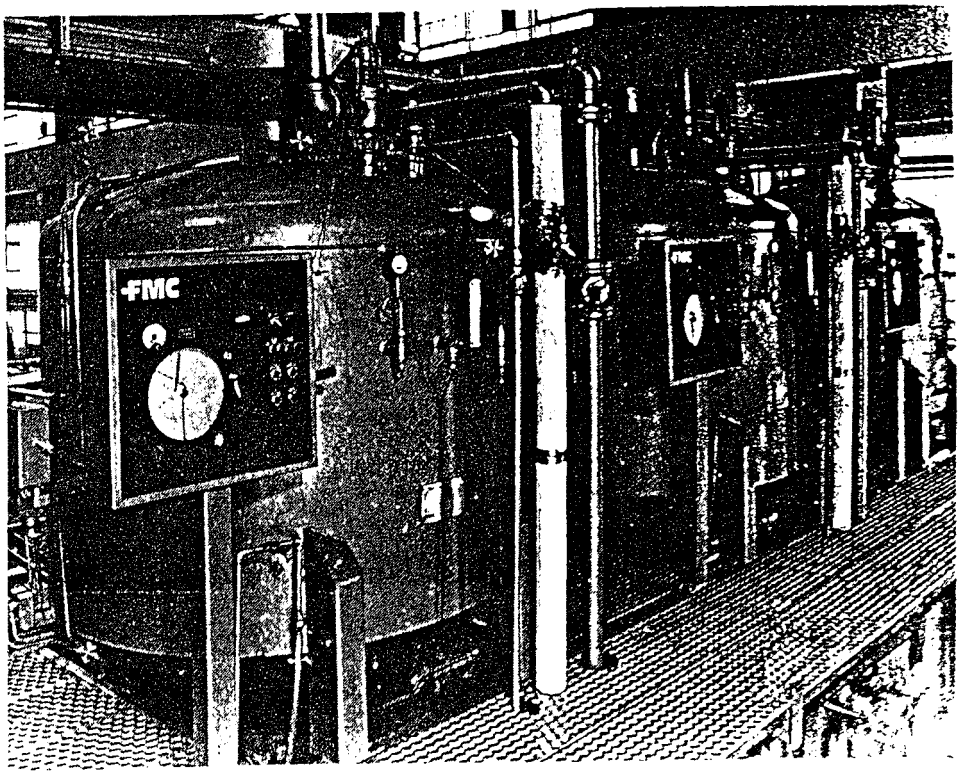


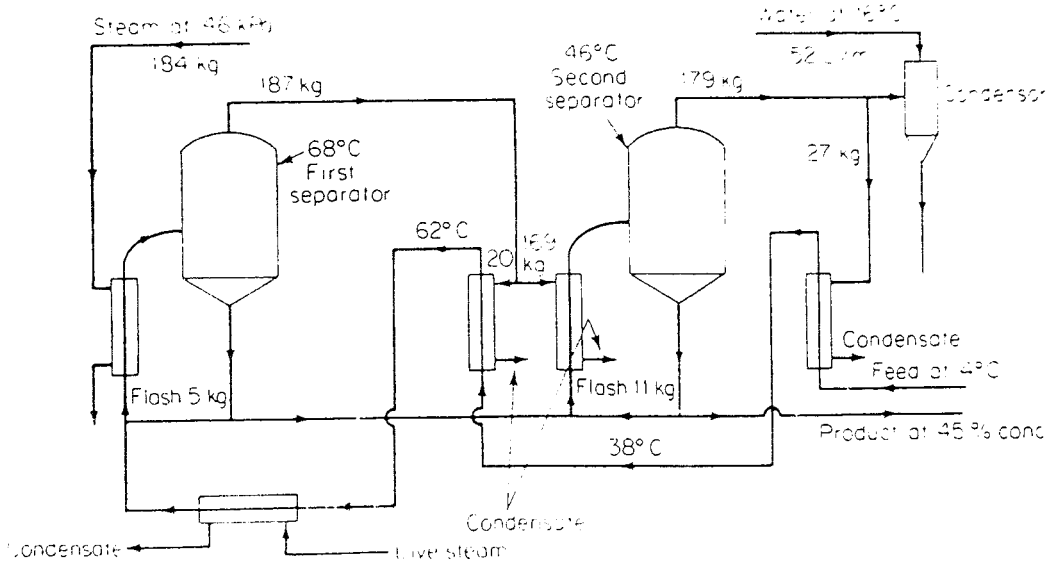
Fig. 25.2. Crateless retort system which consists of one or more pressure vessels mounted above the water tank which is equipped with a submerged conveyor. Containers from the closer are moved by a single conveying system over the top of the pressure vessels and directed into the first vessel ready for loading. Each vessel is prefilled with hot water to cushion the fall of the containers and to maintain the initial temperature during the loading phase. When the vessel is full, the top gate closes and incoming containers continue to the next vessel. The containers remain in steam, controlled at the required temperature, for the necessary sterilization time. *(FMC Corp.)*

CONCENTRATION. Foodstuffs that naturally contain a high percentage of water may be partially dehydrated as a method of preservation. Milk is often evaporated from a solids content of 8.6% to the much more concentrated 45% solids of evaporated milk. Orange juice and other fruit juices are also concentrated before marketing. The usual practice is to reduce the volume to one-third the original volume.

Three processes are available for food concentration: evaporation with evaporators, reverse osmosis, and freeze concentration. Figure 25.3 shows a double-effect evaporator that is used for milk. The three processes are competitive,[7] and the choice depends upon the nature of the food, although evaporation is by far the most economical and common. Reverse osmosis (see Chap. 3) is being used for separation as well as concentration as in the separation of lactose from whey. Other products that are being concentrated in this way are egg whites, fruit juices, and maple syrup.

Food applications for freeze concentration are still very limited because of high cost.

[7]Karel, Fennema, and Lund, *Principles of Food Science*, part II *Physical Principles of Food Preservation*, Marcel Dekker, New York, 1975; Renshaw, Sapakie, and Hanson, Concentration Economics in the Food Industry, *Chem. Eng. Prog.* 78 (5):33 (1982).



CAPACITY, KG/H	
Feed at 8.6% solids	455
Product at 45% solids	87
Total evaporation	368

	PERFORMANCE FACTORS	
	EVAPORATOR GROUP ONLY	EVAPORATOR PLUS LIVE STEAM HEATER
Total steam used, kg/h	184	194
Kilograms of evaporation per kilograms of steam	2.00	1.90
Kilograms of steam per 1000 kg evaporation	500	526

Figures above include heating the cold feed through a temperature rise of 51°C.

Fig. 25.3. Flowchart for a double-effect evaporator with vapor and bleeder heaters.

Among the products that have been reduced in water content in this way are wine, beer, coffee, apple and orange juices, skim milk, and vinegar. This process has the advantage of not destroying color or flavor as happens with heat treatment.

FREEZING.[8] The preservation of fresh foods by freezing has been made possible by the realization that if food can be frozen very quickly (supercooled) and maintained at a low enough temperature to prevent appreciable ice crystal formation, the quality will not be greatly deteriorated and microorganisms will not increase. Ordinary slow freezing produces large ice crystals in the cells of the foods which rupture the cells and cause a breakdown of the structure of the food and allows undesirable enzyme reactions even at low temperatures (−18°C). Inactivation of enzymes by heat treatment (blanching) prior to freezing helps to prevent these unwanted changes.

If the amount of water in a food can be reduced before freezing, the quality of the final product will generally be improved. Concentrated, frozen orange juice is an example of this type of treatment. The reduction in water content before freezing also reduces the volume increase of liquids during freezing.

Foods may be frozen either packaged or unpackaged. Unpackaged food freezes faster, which is desirable, but dehydration may become a serious problem. The actual freezing may be accomplished by either still or forced air, by direct contact with a metal surface cooled by a refrigerant, or by immersion in a liquid refrigerant such as liquid nitrogen. The latter process is the fastest of the methods available.

Freezing does not kill the microorganisms present in food that cause spoilage, but it does inactivate them. However, on thawing the organisms are reactivated, and the food tends to spoil faster than fresh, unfrozen food. Nutrients are not destroyed by freezing.

DRYING. Human beings have preserved food by drying since ancient times. Cereal grains are dried naturally and require little added effort. Sun drying preserves more fruits than are preserved by any other method. Other products that are dried are the various pastas, milk, coffee and tea, and some vegetables, meats, and eggs.

Dried foods are easy to transport and store because they occupy only about one-tenth the volume of fresh food. Microbial growth is controlled because the amount of free water present is not sufficient for growth. Molds will grow if the water content is 12% or higher, although a few molds will grow at 5% moisture. Most bacteria require at least 30% moisture. Grains are dried to 12% moisture and fruits to 16 to 25%. Milk and milk products (nonfat milk, whey, and casein) are usually dried to a very low water content. The nonfat dry milk of commerce contains less than 5% moisture. The nutritive value of dried food is usually unchanged, but the vitamin content is generally reduced.

Sun drying has been used for generations to dry fruits, but many climates are not suitable. It is the cheapest drying method available, but contamination of the product by dust, insects, birds, and rodents is a major problem. When fruits are dried their bright color becomes a dark brown unless the fruit is treated with SO_2 before drying. Because consumers prefer "moist" dried fruit, glycols are used to "rehydrate" and thus soften the harder sun or mechanically dried product without adding moisture, which would allow the growth of microorganisms.

Mechanical driers and the foods for which they are used are shown in Table 25.3. Freeze dehydration utilizes vacuum conditions at the triple point of water so that water molecules

[8]ECT, 3d ed., vol. 11, 1980, p. 171.

Table 25.3 Types of Driers and Food Products

Drier	Product
Drum	Milk, vegetable juices, cranberries, bananas
Vacuum shelf	Limited products of certain foods
Continuous vacuum	Fruits and vegetables
Atmospheric continuous belt	Vegetables
Fluidized bed	Vegetables
Foam mat	Juices
Spray	Eggs, milk, coffee
Rotary	Some meat products; usually not used for food
Cabinet	Fruits and vegetables
Kiln	Apples, some vegetables
Tunnel	Fruits and vegetables
Freeze	Meats, coffee

SOURCE: Desrosier and Desrosier, *The Technology of Food Preservation*, 4th ed., chap 7, Avi, Westport, Conn., 1977.

will pass from the solid to the gaseous phase without passing through the liquid phase. The usual temperature and pressure used in accomplishing this are 0°C and less than 530 Pa. This method is used for foods that are not successfully dried by other methods, such as meat. The time required is 12 to 24 h, and costs are often four times as much as drying by other methods. Odor, color, flavor, and nutritive value, however, are retained to a greater extent than is possible by conventional dehydration.

PASTEURIZATION AND STERILIZATION. Heat treatment, severe enough to completely inactivate microorganisms, changes the taste of food. In many cases the *cooked* taste is not objectionable and the food is acceptable to the consumer in appearance and flavor. Most people, however, object to the taste of boiled or cooked milk. To overcome these objections, processors only partially sterilize milk for human consumption. The process, known as pasteurization and named for Pasteur, who discovered that the cause of much food spoilage is due to microorganisms, is used almost universally to render milk safe. The most common method of pasteurization is the high-temperature short-time (HTST) method which exposes the milk to 73°C for not less than 16 s, followed by rapid cooling. The purpose of pasteurization is to kill pathogenic (disease-causing) microorganisms, thus eliminating food-borne disease, and to inactivate enzymes to improve storage and keeping quality. Because this method does not kill all the bacteria present, the product must be kept under refrigeration until used.

Milk sterilization, i.e., process conditions severe enough to kill or completely inactivate all microorganisms, pathogenic and nonpathogenic, consists of a more intense heat treatment. The sterilized product must be placed in a sterile container under aseptic conditions and sealed. Milk thus treated can be stored for several months at room temperature. Unfortunately, many people complain that it does not taste as good as pasteurized milk. Research is continuing to devise a system of sterilization that does not change the taste.

DASI[9] company has patented a Free Falling Film (FFF) system that they claim eliminates the "burnt taste" of ultrahigh-temperature sterilized milk. The milk is preheated to 65°C, conveyed to a vessel where steam is maintained at 138 to 150°C under pressure. The milk flows from thin slits at the bottom of horizontal feed pipes forming a thin film. Passage

[9]The Competition Heats Up for Fluid Sterilization, *Chem. Week* 129 (16) 37 (1981).

through the vessel is very quick, ⅛ to ¼ s, and the sterilized milk is collected in an air-cooled cone-shaped bottom of the vessel.

There are other milk sterilization systems. Alfa-Laval's heats milk moving through a plastic sleeve which is moving through hot water. The sleeve itself is cut and heat-sealed to form sterile packages. Cherry-Burrel's No-Bac process injects steam directly into the fluid milk.

FERMENTATION. While most food processing and preservation methods are aimed at destroying microorganisms, it is important to remember that not all these organisms are detrimental. Human beings have utilized the action of various microorganisms and yeasts for thousands of years in wine making, bread baking, cheese making, and salting of foods, even though most of that time the actual agents doing the work were unknown. It is important to differentiate between the terms fermentation and putrefaction. Fermentation is decomposition of carbohydrates, while putrefaction involves the action of microorganisms on protein. Fermentation usually produces carbon dioxide but no putrid odor, while putrefaction produces sulfur-containing protein products and hydrogen sulfide. The fermentation industries are discussed in Chap. 31 and produce vinegar, wine, beer, and other alcoholic beverages.

IRRADIATION.[10] The effects of radiation, especially gamma rays, upon various forms of life vary with the complexity of the living organism. Doses of several joules per kilogram (several hundred rads) are lethal to human beings; it requires doses of up to a hundred joules per kilogram (10^4 rads) to kill most insects. Some microorganisms require 10^4 J/kg (10^6 rads). In general, the more complex the organism the more sensitive it is to radiation. Figure 25.4 shows the radiation sensitivity of different organisms. However, it has been shown that radiation can be used to preserve food, especially protein food such as meat, without causing undesirable protein denaturation or appreciably altering the taste, and without leaving any residual radioactivity in the food. With low doses of radiation there is less loss of vitamins in all foods than that seen with canning, freezing, or drying.

[10]Food Irradiation, *Food Eng.* 54 (4) 71 (1982); Karel, Fennema, and Lund, op. cit., chap. 4; Desrosier and Desrosier, op. cit., chap. 13; Paparella, Update on Food Irradiation, *Food Technol./Manag.* 105 (7) 62 (1982).

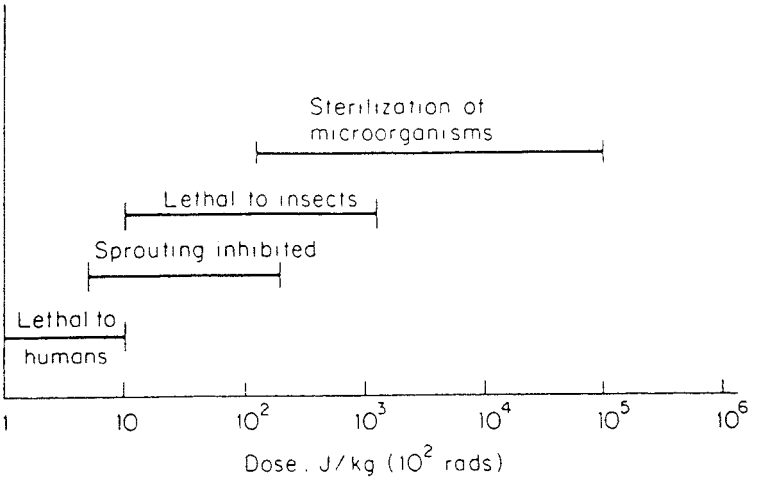


Fig. 25.4. Comparison of radiation sensitivity of different organisms. *(Karel, Fennema, and Lind, Principles of Food Science, Part II, Marcel Dekker, 1975.)*

Worldwide, irradiation has been approved as a safe and acceptable method of food preservation for a wide variety of foods ranging from meat to fresh fruit and vegetables to dry food such as flour and spices. Estimates have been made that up to one-third of the world food supply is destroyed annually by attacks of microorganisms and insects. Irradiation can help to prevent some of this loss. The present recommendation by the Joint Expert Committee on Food Irradiation (JECFI) made up from members from the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) of the United Nations and the International Atomic Energy Commission is that all major categories of food can be safely treated if the dose does not exceed 10^4 J/kg (10^6 rads). The U.S. FDA is considering adopting this standard also. Much interest is being expressed in irradiating fresh fruits and vegetables to kill the Medfly, in preventing potatoes and other root crops from sprouting during storage, and to eliminate the use of nitrites in cured meat.

PACKAGING. The purpose of packaging food is to make it possible to ship and store it far from the place of production and to prevent deterioration during storage by insects, molds, yeasts, microorganisms, and enzymes. For many foods the container is filled before the food is processed. Examples of this are rigid metal cans, glass containers, and plastic pouches. These containers are sealed so that no outside contaminant can enter and cause food spoilage.

Cardboard boxes, usually with inside liners of waxed- or plastic-coated paper, are commonly used for the packaging of dry foods such as cereals, flours, dried fruits, and various convenience mixtures, of which cake and biscuit mixes are examples. For larger quantities of flour the usual packaging is a sack made of finely woven cloth or coated paper.

The advent of food sterilized before it has been placed in its container has necessitated the development of *aseptic* packaging.[11] Five new systems were introduced at the Food and Dairy Exposition in Atlanta, Ga., in November 1981. The advantages of aseptic processing and packaging are much longer shelf-life and the ability to store perishable food, such as milk, without refrigeration. The packages, usually of rigid, rectangular cardboard construction, are sterilized by the use of hydrogen peroxide and heat. In one process the use of ultraviolet light has been added to the peroxide sterilization. These packages require special equipment for forming and filling, which also must be kept sterile.

Another process introduced at the exposition utilizes a plastic container which is fabricated of a multilayered plastic sheet (Fig. 25.5). During fabrication in a sterile chamber the inner layer of the sheet is removed leaving a sterile surface to come in contact with the food. No chemical sterilants are needed as the plastic sheet was heat sterilized during manufacture.

FOOD BY-PRODUCTS

Leather

HISTORICAL. Leather is one of the oldest commodities known. The first leather was made when hides were treated with vegetable extracts to make them weather-resistant. The art of leather manufacturing antedates by centuries any scientific knowledge of the chemistry involved. Probably the greatest single advance in the leather industry was the practical appli-

[11] Aseptic Packaging Fever, *Food Eng.* **54** (1) 59 (1982); Hannigan, Aseptic Package Report, *Food Eng.* **54** (2) 53 (1982).

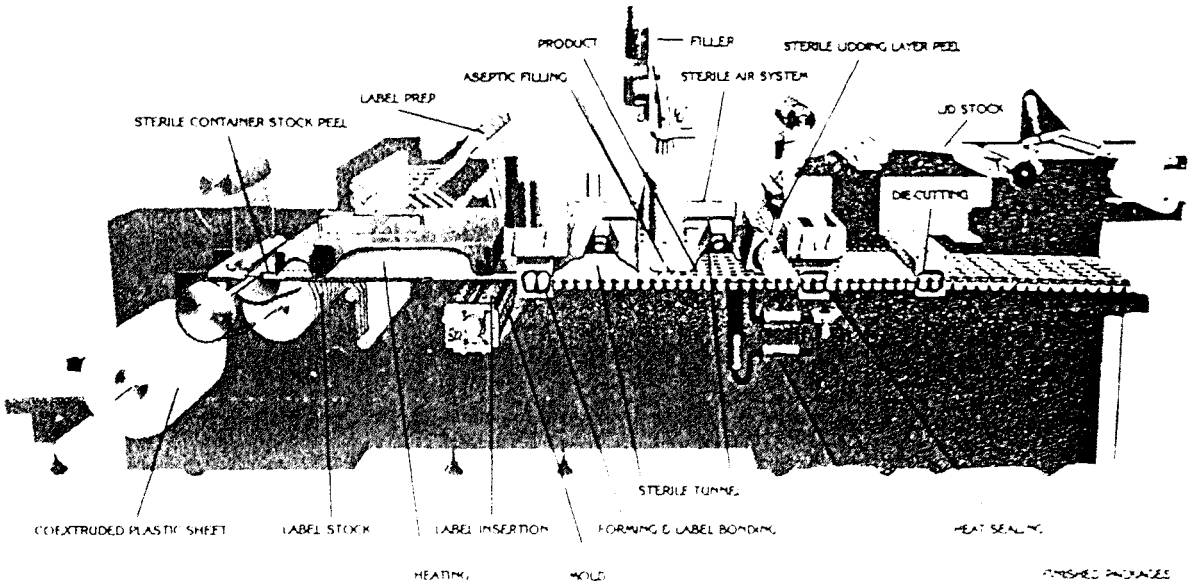


Fig. 25.5. Conoffast's neutral aseptic packaging system for milk, juice, desserts, fruit or vegetable purees, and soups. *(Continental Can Co., U.S.A.)*

cation of the chrome process of tanning introduced in 1893. More than 90 percent of the world's output of leather is chrome tanned.

ECONOMICS AND USES. In 1977 there were 465 U.S. plants manufacturing leather products. Half of the output was used for shoes and the rest for garments, gloves, handbags, belts, etc. In 1981 leather production had a value of $\$2180 \times 10^6$ and the industry employed 20,300 people. Artificial leather and coated fabrics have made heavy inroads on traditional leather markets; over 70 percent of all shoe soles are now synthetic. For example, soles of synthetic rubber and a special high styrene-butadiene resin outwear leather by a wide margin and cost less. Patent leather has been extensively replaced by the superior vinyl plastic. The fact that plastics can be produced in large sheets both eliminates waste in cutting and lends itself to automation. A porous synthetic leather called Corfam was introduced in 1963. A technical but not a commercial success, it is no longer made in the United States. A variety of plastic composites continue to offer competition to leather but fail to displace it for quality or severe applications—such as use in work shoes and boots.

The leather industry is a gross consumer of energy and is classed with other energy-demanding industries such as aluminum, paper, steel, cement, and petroleum. Over 40 percent of the energy used in leather preparation is used for drying the skins, 37 percent in finishing, and 13 percent in beaming and tanning.[12]

MANUFACTURE.[13] Figure 25.6 shows the necessary steps in the manufacture of leather. Both vegetable tanning and chrome tanning operations are shown.

In the chrome tanning process the pickling bath consists of a mixture of salt and sulfuric acid. After pickling, the hides are soaked in a solution of sodium dichromate and then treated with sodium thiosulfate in the reduction drum. From the reduction drum the hide is treated in settling drums with borax to set the chrome salt on the fibers. Washing completes the tanning process.

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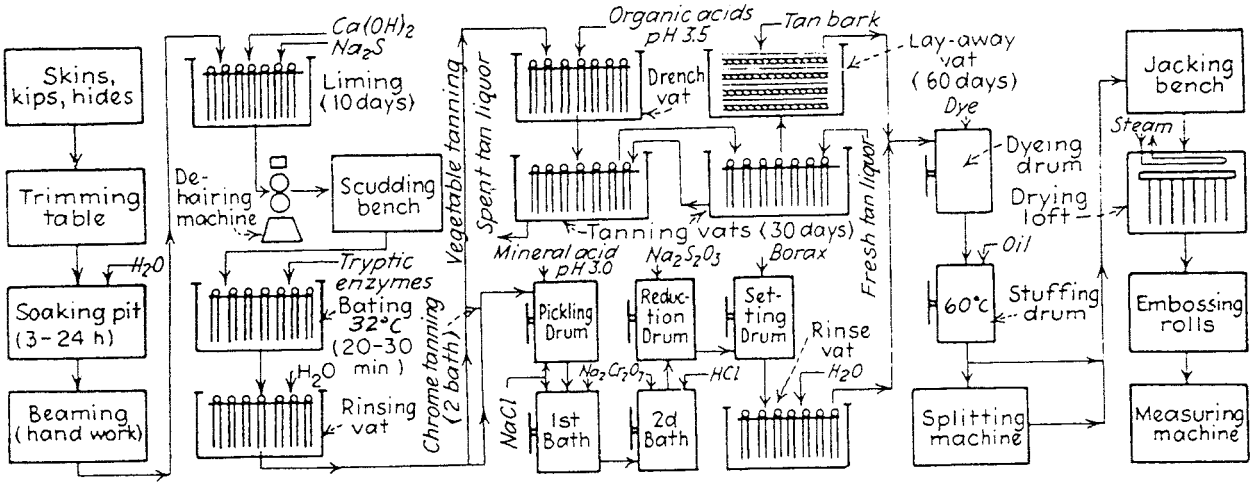
[12]ECT, 3d ed., vol. 14, 1981, p. 220.

[13]For a more complete discussion, see CPI 4, chap. 25.



In order to produce 125 kg vegetable tan or 80 kg chrome tan leather, the following materials and utilities are required:

Hides	100 kg	Oil: Sole	2 kg
Lime	10 kg	Belting	8 kg
Na_2S	2 kg	Harness	20 kg
Water	1665 L	Electricity	8 MJ
Dye	11 kg	Direct labor	4.4 work-h

In addition, for vegetable tan, the following material is added:

Lactic acid	1.2 kg	Tan bark	20 kg	Water	1457 L

For chrome tan, the following material is added:

HCl (30%)	25 kg	$Na_2S_2O_3$	15 kg
NaCl	20 kg	Borax	2 kg
$Na_2Cr_2O_7 \cdot 2H_2O$	5 kg	Water	3330 L

Fig. 25.6. The manufacture of leather.

Vegetable tanning utilizes tannins (complex glucosides of catechols and pyrogallols) obtained from bark extracts of quebracho, eucalyptus, chestnut, and other trees. These tannins react with the collagen fibers of the skins. The pH is regulated by the use of sulfuric acid. The protein in the skin absorbs large quantities of tannin, and the absorbed material fills up the holes and stiffens the leather.

Synthetic tanning agents or *syntans* are condensation products of sulfonated phenols (or higher homologs) and formaldehyde. These are used extensively in the leather industry. Syntans may be classified by use as auxiliary, complementary, or replacement tannins.

Preparation of leather by vegetable tanning requires 2 to 4 months, while chrome tanning requires only 1 to 3 weeks.

Gelatin

Gelatin[14] is an organic nitrogenous, colloidal protein substance whose principal value depends on its coagulative, protective, and adhesive powers. Water containing only 1% high-test gel-

[14]ECT, 3d ed., vol. 11, 1980, p. 711; Ward and Courts (ed.), *The Science and Technology of Gelatin*, Academic, New York, 1977; *McGraw-Hill Encyclopedia of Science and Technology*, vol. 1, McGraw-Hill, New York, 1982, p. 114.

atin by weight forms a jelly when cold. There is little, if any, chemical or physical relationship between gelatin and other materials bearing this name, such as blasting gelatin, formed by mixing collodion cotton with nitroglycerine, or Japanese gelatin, also known as agar-agar, a mucilaginous substance extracted from seaweed. Animal gelatin is obtained by hydrolysis from collagen—white fibers of the connective tissues of the animal body, particularly the skin (corium), bones (ossein), and tendons.

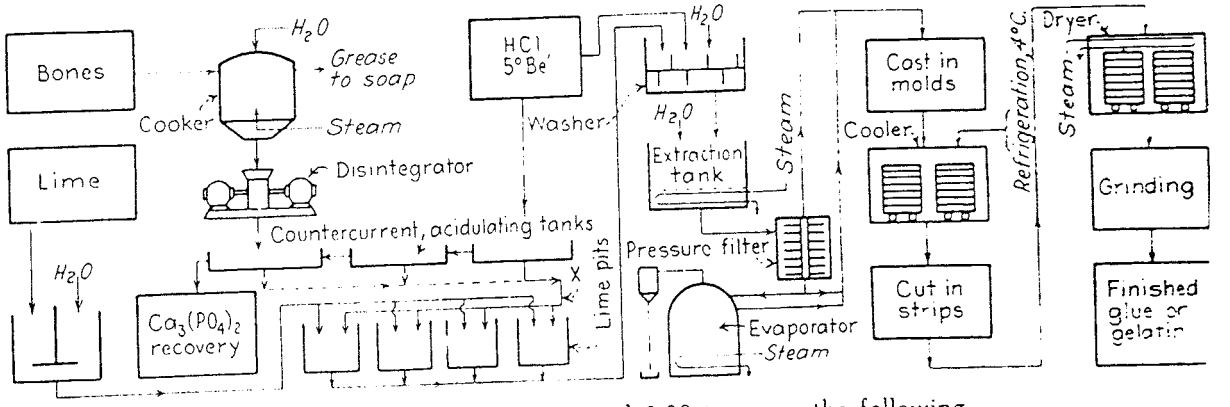
USES AND ECONOMICS. The industry recognizes two different kinds of gelatin, types A and B. Type A is acid processed and type B is lime processed. Food uses account for almost 19,000 t/year,[15] mostly type A. More than 55 percent of all the type A gelatin produced is used for food. Other uses of gelatin are for pharmaceutical capsules, as an emulsifier (7800 t/year), and for photographic film (7000 t/year).[16]

MANUFACTURE. Type A gelatin is made from skins which are first washed, and then swollen for 10 to 30 h in HCl, H_3PO_4, or H_2SO_4 at pH 1.0 to 3.0. After swelling, the skins are washed, the pH adjusted to 3.5 to 4.0, and then extracted with hot water. Four or five extraction tanks are used, and the extractive water becomes progressively hotter in each succeeding tank. The first extraction is at 55 to 65°C and the last at 95 to 100°C. Each extraction requires 4 to 5 h. After the last extraction is completed the liquid is degreased, filtered, deionized, and then concentrated in two stages to 30 to 40% solids by continuous vacuum concentration. The high-solids solution is chilled, cut into "noodles," and dried below 60°C on a continuous wire-mesh belt. The dried material is ground and blended with other gelatins to produce the desired specifications.

Type B gelatin is made from bones and sometimes skins and hides as shown in Fig. 25.6. The degreased bones are demineralized with 4 to 7% HCl over a 1- to 2-week period. After washing, the bones are agitated daily for 3 to 16 weeks in a lime slurry in lime pits or tanks.

[15] t = 1000 kg.

[16] Getting New Markets to Gel for an Old, Old Product, *Chem. Week* 128 (8) 46 (1981).



To produce 1 t of gelatin, 1.67 t of $Ca_3(PO_4)_2$, and 0.08 t grease, the following materials and utilities are required:

Bones	3.03 t	Steam	200 kg
Hydrochloric acid	1.14 t	Electricity	218 MJ
Lime	0.76 t	Direct labor	7 work-h

Fig. 25.7. Flowchart for glue and gelatin manufacture. NOTE: Manufacture of glue and gelatin differ largely in that poorer grades of raw materials and higher extracting temperatures are used for the former. Glue is more completely hydrolyzed than gelatin. In addition to bones, skins, hides, sinews, hide scrap, fleshings, fish stock, etc., may be used, in which case, after washing they are introduced at X.

When the lime treatment is complete, the mix is washed for 15 to 30 h, acidified to pH 5 to 7 with HCl, H_3PO_4, H_2SO_4, or $HC_2H_3O_2$ and extracted and concentrated as for Type A. See Fig. 25.7.

Both of these processes require the use of stainless steel for most of the equipment, although the liming tanks may be of concrete or wood. The production of edible gelatin must meet the requirements of the Food and Drug Administration, and the manufacture of photographic gelatin is much more complicated than that for producing other gelatins. It is for this reason that the price of photographic gelatin is nearly twice that of the edible variety. All the ingredients used must be very pure, and specifications for the final product are very rigid.

Adhesives

There are hundreds of adhesive[17] preparations on the market today, supplemented by hundreds of available formulations, which are capable of holding materials together by surface attachment. Although the basic components of the products are generally obtainable their specific combinations are not always known to the public. Many compositions are protected by patents. In 1980 adhesive shipments were valued at nearly $\$2000 \times 10^6$.[18] Modern adhesives may be classified by one of several methods; for example, their use in bonding various types of material, such as structural adhesives, or their composition, based on the principal ingredient, such as thermoplastic resin. Since the more-or-less general term "adhesives" embraces many types, they are discussed under their composition.

HISTORICAL. Animal glue is the oldest type of adhesive, having been known for at least 3300 years. Its manufacture began in the United States in 1808, and it has been an important article of commerce for more than 150 years, although practical application in broad industrial fields had to await progress in colloid and protein chemistry and the development of standard testing methods. Casein and starch adhesives became of commercial importance more than a generation ago, and soybean-protein adhesive in the last 50 years; synthetic resin adhesives were developed after 1940.

ANIMAL GLUES. The manufacture of glue is almost identical with the manufacture of gelatin (Figs. 25.7 and 25.8). The procedures include grinding bones; cutting hides and scraps into small pieces; degreasing the material by percolating a grease solvent through it; liming and plumping; washing; making several extractions by hot water; filtering liquors; evaporating, chilling, and drying the jelly slabs in a tunnel. When dry, the slabs of glue are flaked or ground, blended, graded, and barreled or bagged for shipment.

OTHER PROTEIN ADHESIVES. Fish glues are liquid glues made from waste materials of cod, haddock, cusk, hake, and pollock, and have practically the same applications as other animal glues. Casein, a milk-derived protein, is the basis of another large class of adhesives and can be made both water- and non-water-resistant. Casein adhesives are widely employed in the woodworking industry and in the manufacture of drinking cups, straws, and ice cream containers. Soybean protein adhesives, although similar in properties to casein adhesives, are cheaper but not so good. The two are generally employed in combination, particularly in the veneer field, thus permitting a reduction in glue costs. Albumin adhesives, from both egg and

[17]*Skeist Handbook of Adhesives*, 2d ed., Van Nostrand Reinhold, New York, 1977.

[18]Storck, Adhesives Use to Continue Modest Climb, *Chem. Eng. News* 59 (5) 8 (1981).

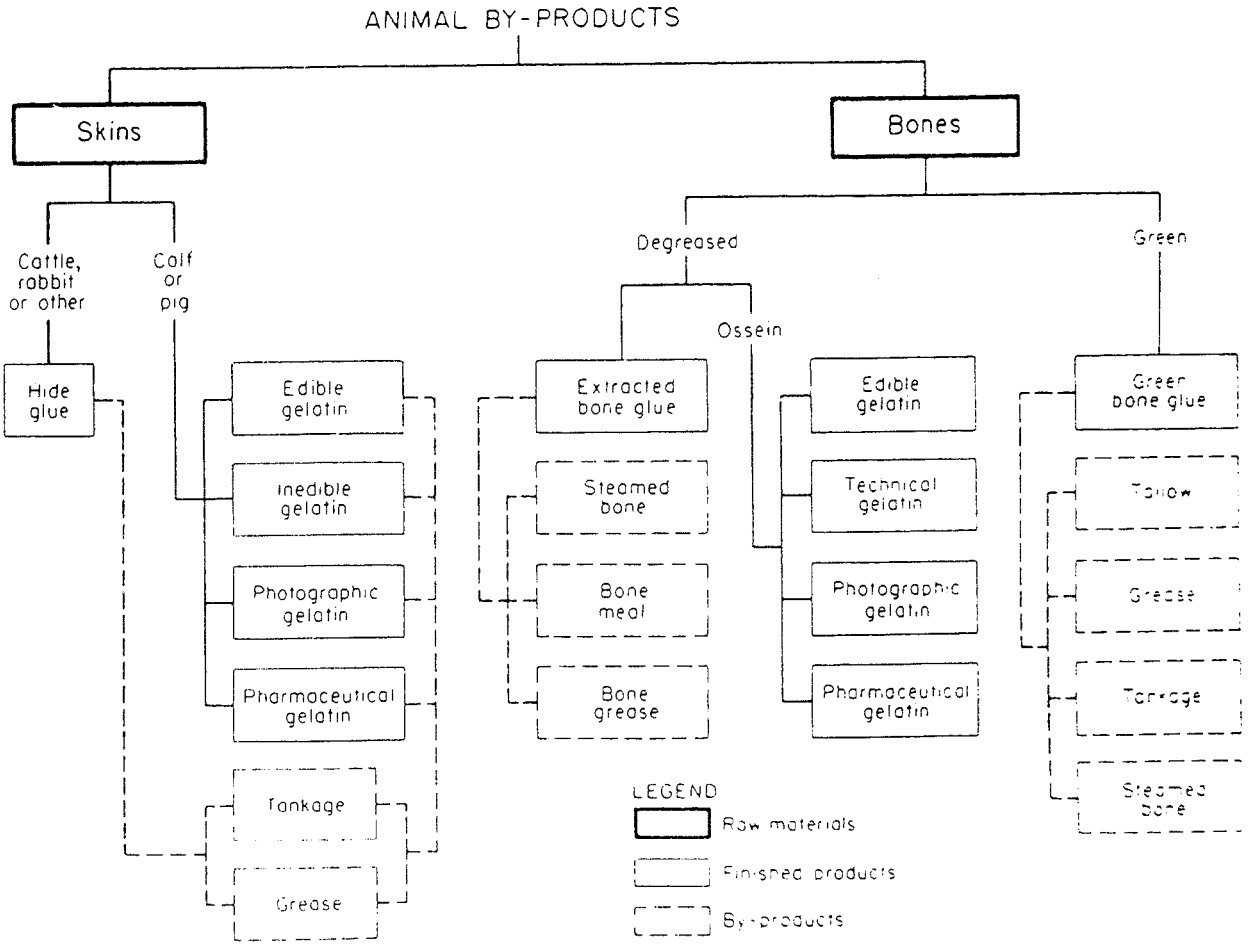


Fig. 25.8. Animal glue and gelatins. *(Adapted from U.S. Tariff Commission Report 135.)*

blood, find specialized uses where low film strength is unimportant, yet water resistance is. The attachment of cork pads to crown bottle caps is one of these applications. Zein, a corn protein, is used to a small extent as an adhesive, particularly in combination with other bases. Peanut protein hydrates are suitable for making gummed tape and flexible glues for boxes and books

STARCH ADHESIVES. Starch adhesives, or glues, were first used in large-scale industrial application approximately in the 1910s. The chief kinds on the market today are made from cornstarch, tapioca flour, wheat flour, and potato starch. Starch adhesives may be applied cold and do not have the undesirable characteristic odors of some animal glues. This is one of their chief advantages over animal glues, although most of them have the disadvantage of less strength and lower water resistance than animal glues. Starch adhesives are less costly than synthetic-resin adhesives. Native starch is widely employed as an adhesive for veneer, plywood, and corrugated cartons and laminated boards where water resistance is not important. Incorporated with 5 to 15% resins, such as urea-formaldehyde, it is used for cartons where water resistance is important. Through enzyme conversions it is a base for many liquid adhesives. Native starch is the raw material for hydration to dextrins and British gums; these are modified glues for glass, metal, and wood, cartons, laminated boards, and padding glues. Tapioca dextrin is the adhesive used for postage stamps.

Native starches are prepared from grains or roots (Chap. 30). Dextrins are made by heating a dry starch with dilute acid, causing partial hydration. British gums result from heating native starch with small amounts of catalysts; they are gummier and more adhesive than dextrins. In the manufacture of starch adhesives, dextrins, British gums, or starches are rarely

used alone. Many chemicals may be admixed as indicated. Borax increases viscosity, gumminess, rate of tack, and speed of production.

SYNTHETIC-RESIN ADHESIVES. The synthetic-resin adhesives are used where water resistance is required and/or other special conditions must be met. They may be classified as solvent-borne systems, water-borne systems, nonvolatile solids and liquids, hot melts, powders, radiation curable systems, two-part systems, and reactive systems. Water-borne systems, both naturally derived and synthetic-resin based, represent more than two-thirds of the adhesive demand. Another classification is by method of setting: solvent releasing, hot melt, and pressure sensitive.[19]

Chemically, synthetic adhesives are of two types, those which are merely adhesives and those which form primary bond linkages with the materials being bonded. One classification includes rigid thermosets, rubbery thermosets, thermoplastics, copolymers and polymer mixtures, and inorganic adhesives. Application by the evaporation of volatile solvents (except water) is rapidly diminishing because of air pollution problems.[20] Hot-melt applications are increasing. Some compositions require the mixture of two stable solutions for activation; others are activated by oxygen or moisture in the air. Specially coated tape removal activates others. Some pressure-activated tapes are used.

Rigid thermosets include epoxies, silicones, polyesters, cyanoacrylates (very fast setting[21]), and phenolic, urea-formaldehyde, and resorcinol-formaldehyde resins. Heat and chemical resistance are usually good; some have excellent water resistance.

Rubbery Thermosets. Silicones, urethane, butyl, and polysulfide rubbers are used. Many of these are used as sealants, i.e., fastening materials together to exclude weather or gases, but bond strength is not highly important. Resistance to water, sunlight, and vibration for long periods is essential.

Thermoplastics. These include vinyls, polystyrenes, acrylates, polyamides, rubber-based adhesives, rosin, animal glues, and starch and dextrin glues. Most hot-melt, nonsolvent glues belong to this group.

Copolymers and Mixtures. These are formed to obtain better properties than those possible with single components, e.g., good adhesion and high-temperature resistance. Epoxy with nylon, phenolics, polyamides, silicones, and urethanes, nitrile-phenolics, and vinyl-phenolics are all used.

MISCELLANEOUS ADHESIVES. *Inorganic adhesives* include glasses and ceramics for very high temperature service and sodium silicate which is used for manufacturing corrugated boxes.

Other adhesives include asphalt, sulfur, shellac, miscellaneous natural gums and mucilages, and a variety of cellulose esters dissolved in volatile solvents; they are widely used in the home and office. There is no all-purpose adhesive. Many types of industrial fasteners are being economically replaced with adhesives. Modern aircraft and automobiles, and even spacecraft, use adhesives for assembly, saving money and reducing weight.

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[19]Ellerhorst, Industrial Adhesive Market, *Adhes. Age* 25 (1) 43 (1982); Wake, *Adhesion and the Formulation of Adhesives*, Appl. Sci. Publ., London, 1976; Skeist, op. cit.

[20]Packagers Bend to New Solvent Rules, *Chem. Week* 127 (1) 29 (1980).

[21]Millet, Cyanoacrylates, *Adhes. Age* 24 (10) 27 (1981).

FOOD PROCESSING EQUIPMENT

SANITARY DESIGN AND MATERIALS OF CONSTRUCTION. Processing equipment for food is similar to that for other processing. Liquids, solids, and combinations must be handled without deterioration of the product or damage to the equipment. Sanitary conditions are a necessary additional consideration beyond normal unit operation. Chemical and biological properties usually play a more predominant role than mechanical properties in the design of equipment for the food industry. In addition to the usual problems associated with corrosion-resistant materials, the character and toxicity of the corrosion products must be considered. Good appearance must also be maintained. The pH of fluid products is the major factor in materials selection. Products containing vinegar and salt are among the most corrosive materials. The most acidic goods commonly processed are cranberry juice, lemon juice, sweet pickles, and cranberry sauce; all are below pH 3.0. Few foods are alkaline; generally they are below pH 8.0. Crab meat is pH 6.8, and some chicken preparations are pH 6.5. Time, temperature, pH, product roughness, velocity of flow, and surface condition (smoothness and previous usage) all affect the rate at which equipment is attacked by the material it contains.

Stainless steel, which owes its corrosion resistance to a passive oxide layer on its surface, is widely used. For acidic foods, Type 316[22] is usually required. Glass and glass-coated materials, plastics, and aluminum are also being used for food processing equipment. The use of copper, tinned copper, and zinc is almost obsolete.

Three associations, the International Association of Milk, Food and Environmental Sanitarians, the Dairy Industry, and the Food and Industry Supply Association, are known as Three-A and have set standards for design of equipment to ensure sanitary conditions. Some of the special features are:

1. Material, in general, should be 18-8 stainless steel with a carbon content of not more than 0.12%, or equally corrosion-resistant material.
2. The gage of metal should be sufficient for the various applications.
3. Product surfaces fabricated from sheets should have a No. 4 finish or equivalent.[23]
4. Square corners should be avoided. Minimum radii are often specified, e.g., a storage tank must have inside corners of 6.4 mm for permanent attachments.
5. No threads should be in contact with food. Acme threads should be used.
6. Surfaces should be sloped to provide drainage.
7. Designs should permit interchangeability of parts.

Halogens cause pitting in stainless steel, especially free chlorine dissolved in small droplets of water on the surface. Exposure to chlorine, bromine, or iodine used for sanitizing should be limited to 20 or 30 min and temperatures kept below 30°C. A better solution is to use glass or glass-coated or plastic-coated equipment for this service.

CLEANING. Manual cleaning involves drudgery under poor working conditions and utilizes as much as 50 percent of the labor used in a plant. Cleaning in place has eliminated the problem and is a major development. Three-A standards for cleaning in place are:

1. Using alkali or acid solutions appropriate for the product and equipment surface.
2. Providing a time of exposure of 10 to 60 min to remove substances without damage to the metal.

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[22]See Perry, 5th ed., p. 23-15 for steel type systems.

[23]Surface finishes are graded from No. 1 to No. 8 with 8 being most highly polished. In use, finishes above 4 generally reduce spontaneously to 4.

3. Utilizing a velocity of flow of 1.5 m/s (1 to 3 m/s).
4. Maintaining a slope of surface and tubing to provide for drainage (5 to 10 mm/m).
5. Avoiding dead ends for flows.
6. Using connections and joints that are cleanable (welded joints, clamp-type joints, appropriate gaskets).

Stainless steel is remarkably resistant to corrosion but, in contact with other metals, electrolytic cells can be formed which accelerate attack. Graphite packing in pumps is an often overlooked source of electrolytic corrosion. Small pockets of stagnant material, crevices in which materials stagnate, and incomplete cleaning can yield spots where stainless may be attacked. Stainless should not be joined directly to other metals.

Material adhering to a stainless-steel surface should be removed with the least abrasive material that can do the job. Normally, a mild abrasive can be used or a stainless-steel sponge for more aggressive cleaning. Metal sponges of dissimilar metal should not be used, because particles of metal adhering to the surface may set up corrosion cells. After cleaning, the surface should be washed with hot water and left to dry. Sanitization (often incorrectly called sterilization) with 200 ppm chlorine solution should be done 30 min before use, not immediately after cleaning. This procedure is followed to avoid corrosion.

CONTROLS. The food industry is a labor-intensive operation, and increasingly high costs of labor have made process improvements almost a necessity. Continuous processes are replacing batch operations in more and more plants resulting in lower processing costs and greater uniformity. With this development the need for automatic controls has increased. Computer controls and microprocessors are still not fully utilized, but it is expected that they will become increasingly important.[24] They have been used successfully in sugar, mayonnaise, cheese, and pet food processing plants, among others. In the mayonnaise plant, the accurate control allows continuous production and feed to the packaging line without having any emulsion problems. The cheese plant uses a process control computer to monitor and regulate the entire process; this results in total butterfat control and thus better yields, reduced culture costs, and a total inventory accounting. Quality control is greatly improved by computer control.

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[24]New Incentives for Automatic Control, *Food Eng.* **54** (2) 77 (1982); The Microprocessor Marches On, *Food Eng.* **54** (4) 119 (1982).

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Chapter 3

Sugar and Starch Industries

Carbohydrates, sugars and starches, are major foods for humans that are synthesized by plants using carbon dioxide and water from the atmosphere. These serve as the principal foodstuffs for animals, including humans, and have considerable promise as major chemical raw materials. There is much political demand to convert agricultural surpluses into materials, such as motor fuels, in which the country is deficient, but experimentation over a 50-year period has failed to find an economical approach. Rising petroleum prices make the goal seem nearer. As foods, their use remains extremely important.

SUGAR

Humans desire sweetness in their diet and nature provides it from several sources. The average person in the United States consumes 32 kg of sugar per year, but this amount has been slowly diminishing. The world average is only one-third of this but is increasing. Sugar is not prized for its sweet taste alone, for it supplies about 13 percent of the energy required for existence. As a result, sugar production and refining is a huge industry, consuming 8.3×10^6 t of sugar in the United States alone in 1982. The total world sugar production is estimated[1] at 95.8×10^6 t.[1a]

HISTORICAL. It is difficult to determine just when sugar first became known to humankind but it probably traveled from New Guinea to India many centuries before Christ. Methods for extracting and purifying the sugar from the cane were very slow in being developed, but we find a record of crude methods having been brought from the east to Europe about 1400. The sugar trade between Asia and Europe was one of the most important commercial items in the early centuries. Sugar was first extracted in North America in 1689, using cane from the West Indies, and in 1751 cane was grown on the continent. From that time on, the industry increased steadily, both in size and in quality of product. Steam-driven crushing and grinding roller mills were introduced in the latter part of the eighteenth century; the vacuum pan was invented by Howard about 1824; bone-char decolorization was employed for the first time in 1812. Multieffect evaporation was proposed about 1834, and the first suspended centrifuge was developed by Weston in 1852. The use of granular activated carbon and ion-exchange processes to remove color and ash has become common. Evaporation, adsorption, centrifugation, and filtration were from the beginning the important and necessary steps in

[1] *Sugar J.* 44 (9) 8 (1982).

[1a] t = 1000 kg.

the manufacturing sequences, and much of our knowledge of these methods came from their application in the sugar industry. This study of the functioning of evaporation, adsorption, centrifugation, and filtration as used in sugarmaking helped to establish the generalized concept of unit operations.

In 1747 *beet sugar* was discovered, but it was not introduced into the United States until 1830, and no successful plants were operated until 1870. A great deal of time, effort, and money were expended in bringing the more complicated beet-sugar industry to the point where it could compete with the cane-sugar industry. The various tariffs imposed on raw cane-sugar imports, among other things, are responsible for the continuance of both the beet-sugar and the domestic cane-sugar industries.

The first preparation of *dextrose* in 1811 led to the development of the corn-sugar industry in this country. The first manufacturing began about 1872, the product being liquid glucose. It was not until 1918, however, that appreciable quantities of pure, crystalline dextrose were produced. The most recent major change in the industry was the introduction of high-fructose corn-derived sweetener (HFCS) which became commercial about 1970. This made available a high-quality sweetening material which made corn competitive with cane and sugar beets as a major source of sweetener.

At the start of the present century, the Bergius process for the production of sugar by *saccharification,* or hydrolysis, of wood received its first industrial trial. As far as the United States is concerned, these acid hydrolysis processes, although chemically feasible, have generally proved economically unsound, because of the abundance and low price of starch and sugar; however, they seem to be increasingly promising. Studies with cellulase enzyme conversions to convert wood wastes to glucose to be fermented to give alcohol for use as motor fuel also appear promising. The changing pattern of nutritive sweetener deliveries is shown in Table 30.1.

USES AND ECONOMICS. In 1982, about 8.3×10^6 t of sugar was consumed in the United States. Total nutritive sweeteners, however, totaled 12.8×10^6 t. Of this total, 36 percent came from corn, 33 percent from beets, and 31 percent from cane.[2] Refined sugar sold in the

[2]*Statistical Abstract of the United States,* 102nd ed., 1982, and U.S. Agricultural Outlook Conference, 1980; *Food Eng.,* 54 (7) 77 (1982).

Table 30.1 Nutritive Sweetener Deliveries in the United States (in thousands of metric tons of dry substance)

Year	Sucrose	Corn Syrup	Dextrose	HFCS	% Sweetner from Corn
1970	9484	1305	427	68	16
1975	8753	1718	495	483	24
1977	9430	1764	414	944	25
1979	9138	1823	391	1546	29
1980	8773	1886	399	1955	33
1981	8422	1924	407	2432	36
1982	8273	1909	363	2273	36
1985°	7727	2000	409	3182	43

°Estimated.

SOURCES: *Sugar J.* 43 (8) 13 (1981); *Food Eng.* 54 (7) 77 (1982).

United States is utilized as follows;[3] bakery products, 12.5 percent; beverages, 23.7 percent; confectionery, 8.9 percent; hotel and restaurant use, 1 percent; ice cream and dairy products, 4.6 percent; jams, jellies, and preserves, 6.5 percent; other food uses, 4.7 percent; nonfood uses, 1.2 percent; sold by retail grocers, 12.2 percent; and sold by sugar jobbers, 19.9 percent. HFCS has made inroads into all these markets except confections as a major replacement for sucrose. Both sucrose and HFCS are sold in large quantities in bulk and as syrups.

Nonfood uses of sugar are very few and constitute only a small amount of the total output. They include the use of sugar as a sucrose octaacetate, a denaturant in ethyl alcohol; as sucrose diacetate hexaisobutyrate and octabenzoate, plasticizers; as mono- and difatty acid esters for surfactants, allyl sucrose; and as a raw material for the manufacture of glycerol and mannitol. Dextran, a polysaccharide produced from sucrose by certain bacteria, is a very effective plasma volume expander. Administered by intravenous infusion, it relieves shock and prevents loss of body fluids after extensive burns or other wounds. Other uses for sucrose derivatives are under investigation.

No other crystalline organic product of comparable purity (99.86% anhydrous basis) has been offered on the market for so low a price as sugar and in such large volume. This, however, is merely a reflection of the progress and growth in refining methods due to applied chemical engineering within the industry, which has succeeded in reducing the price from the $8.80 per kilogram in 1796 to its present level of about 81 cents per kilogram. With corn at $12.80 per 100 kg, corn sweetener costs under 33 cents per kilogram to produce.

Manufacture of Sugar

The major processing methods used for refining cane sugar today have been worked out for many years and are unlikely to change drastically soon. Alterations to conserve energy and perhaps reduce the use of some reagents are to be expected, but major process changes seem unlikely.

CANE. Sugarcane is a member of the grass family. It has a bamboolike stalk, grows to a height of from 3 to 5 m, and contains 11 to 15% sucrose by weight. The sources of the raw cane refined in the United States are shown in Table 30.2. The cane is usually planted with cuttings from the mature stalks, which sprout and produce a number of new stalks. As many as seven successive crops, or ratoons, may be obtained from a single planting, provided conditions are favorable. The approximate period of growth of the cane in Cuba is 12 to 15 months, and nearly twice this in Hawaii and Peru. In Louisiana and Florida the growing season is 6 to 9 months. Harvesting is done by hand with machetes or by mechanical cutters following burning to remove the leaves. The workers cut off the stalks close to the ground and top the cane. The cane is loaded on tractor-pulled cane carriers and hauled to the raw-sugar plants, or centrales. There can be no delay in transporting the freshly cut cane to the factory, because failure to process it within less than 24 h after cutting causes loss by inversion to glucose and fructose.

The production of raw cane sugar at the factory is illustrated in Fig. 30.1 and may be divided into the following unit operations and chemical conversions:[4]

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[3]*Commodity Yearbook*, Commodity Research Bureau, New York, 1981; Agricultural Outlook Conference, 1980.

[4]Birch and Parker, *Sugar: Science and Technology*, Appl. Sci. Publ. London, 1979; also ECT, 2d ed., vol. 19, 1969, p. 166.

Table 30.2 Raw Sugar Suppliers to the United States (in thousands of metric tons)

Supply Area	1958	1978	1979	1980
U.S. beet	2013	2907	2901	2701
U.S. cane (mainland)	522	1179	1120	1918
Hawaii	572	917	859	912
Puerto Rico	748	47	43	162
Philippines	891	757	375	372
Dominican Republic	80	667	742	559
Peru	80	204	172	47
Mexico	61	48	55	—
Brazil	--	546	1147	769
All other countries	3134	2037	2061	2339
Total	8101	9309	9475	9779

SOURCE: *Agricultural Statistics 1981*, United States Department of Agriculture.

The cane is first washed to remove mud and debris.

The cane is chopped and shredded by crushers in preparation for removing the juice.

The juice is extracted by passing the crushed cane through a series of mills, each of which consists of three grooved rolls that exert heavy pressure. Water and weak juices may be added to help macerate the cane and aid in the extraction.[5] About 93 percent of the juice is extracted

[5]As with sugar beets, sugar is being extracted from the chopped cane by continuous countercurrent extraction with hot water in diffusers, *Chem. Eng.* 82 (3), 32 (1975).

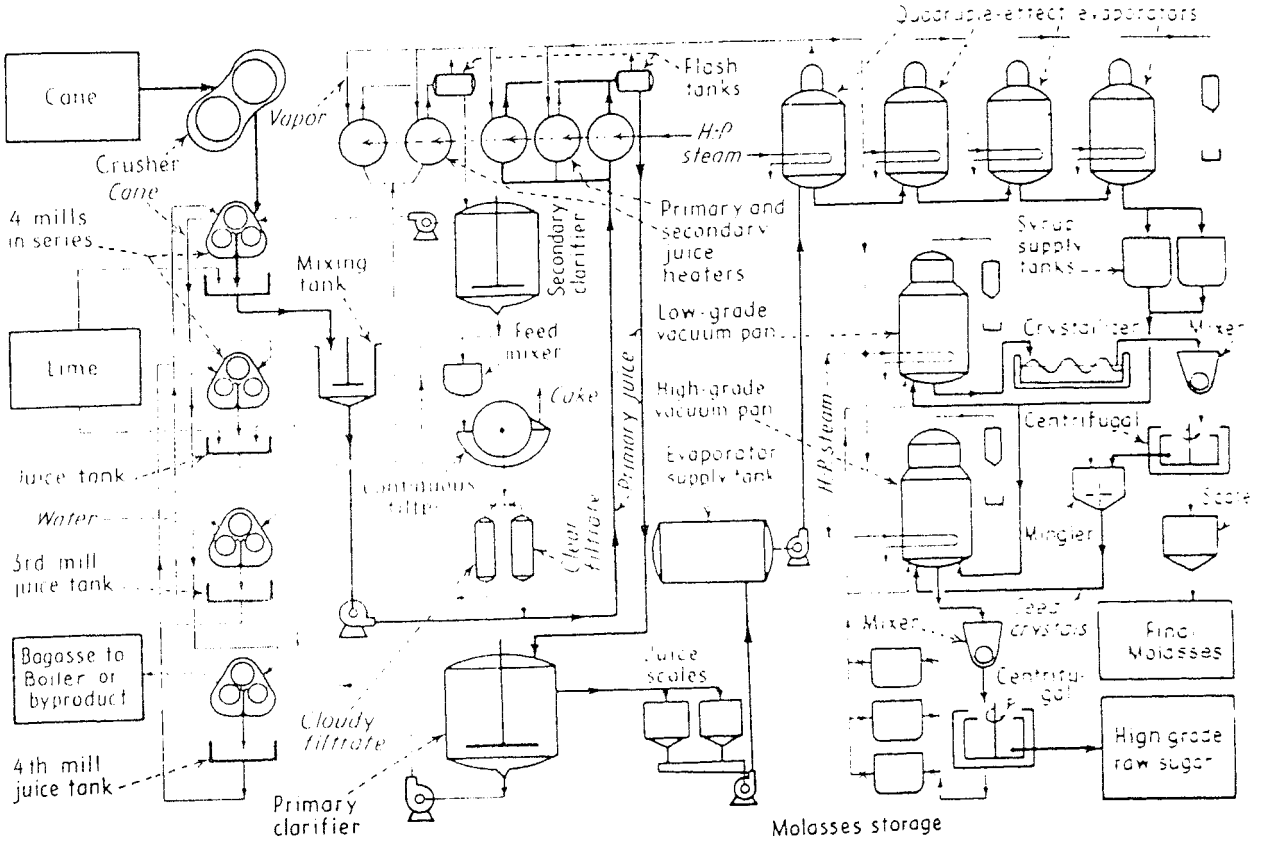

Fig. 30.1. Flowchart for the manufacture of raw cane sugar.

from the cane. The spent cane (bagasse) is either burned for fuel or used to manufacture paper, hardboard, or insulating material.

The juice is screened to remove floating impurities and treated with lime to coagulate part of the colloidal matter, precipitate some of the impurities, and change the pH. Phosphoric acid may be added because juices that do not contain a small amount of phosphates do not clarify well. Lime in slight excess over that theoretically required to precipitate all the phosphate is then added.

The mixture is heated with high-pressure steam and settled in large tanks called *clarifiers* or in continuous settlers or thickeners.

To recover the sugar from the settled-out muds, continuous rotary-drum vacuum filters are generally used. The cake constitutes 1 to 4% of the weight of cane charged and is used as manure.

The filtrate, a clarified juice of high lime content, contains about 85% water. It is evaporated to approximately 40% water in triple- or quadruple-effect evaporators[6] to a thick, pale-yellow juice.

The resulting thick juice goes to the first of three single-effect vacuum pans, where it is evaporated to a predetermined degree of supersaturation. Sugar-crystal nuclei are added (shock seeding) and, by the addition of thick juice and controlled evaporation, the crystals are grown to the desired size in these "strike" pans. At this optimum point, the pan is mostly filled with sugar crystals with about 10% water. The mixture of syrup and crystals (massecuite) is dumped into a crystallizer, which is a horizontal agitated tank equipped with cooling coils. Here additional sucrose deposits on the crystals already formed, and crystallization is completed.

The massecuite is then centrifuged to remove the syrup. The crystals are quality high-grade raw sugar, and the syrup is re-treated to obtain one or two more crops of crystals. The final liquid after reworking is known as blackstrap molasses.

The raw sugar (light brown in color), containing approximately 97.8% sucrose, is shipped in bulk to the refinery, frequently outside the country of origin.

The molasses is shipped to the United States and other countries in full-tank steamers and is used as a source of carbohydrates (a decreasing use) for cattle feed and for citric acid and other fermentations (Chap. 31).

CANE-SUGAR REFINING. Raw sugar is delivered to the refineries in bulk. Figure 30.2 illustrates the following sequences in the refining of cane sugar.[7]

The first step in refining is called affination, wherein the raw-sugar crystals are treated with a heavy syrup (60 to 80° Brix)[8] in order to remove the film of adhering molasses. This strong syrup dissolves little or none of the sugar but does soften or dissolve the coating of impurities. This operation is performed in minglers, which are heavy scroll conveyors fitted with strong mixing flights.

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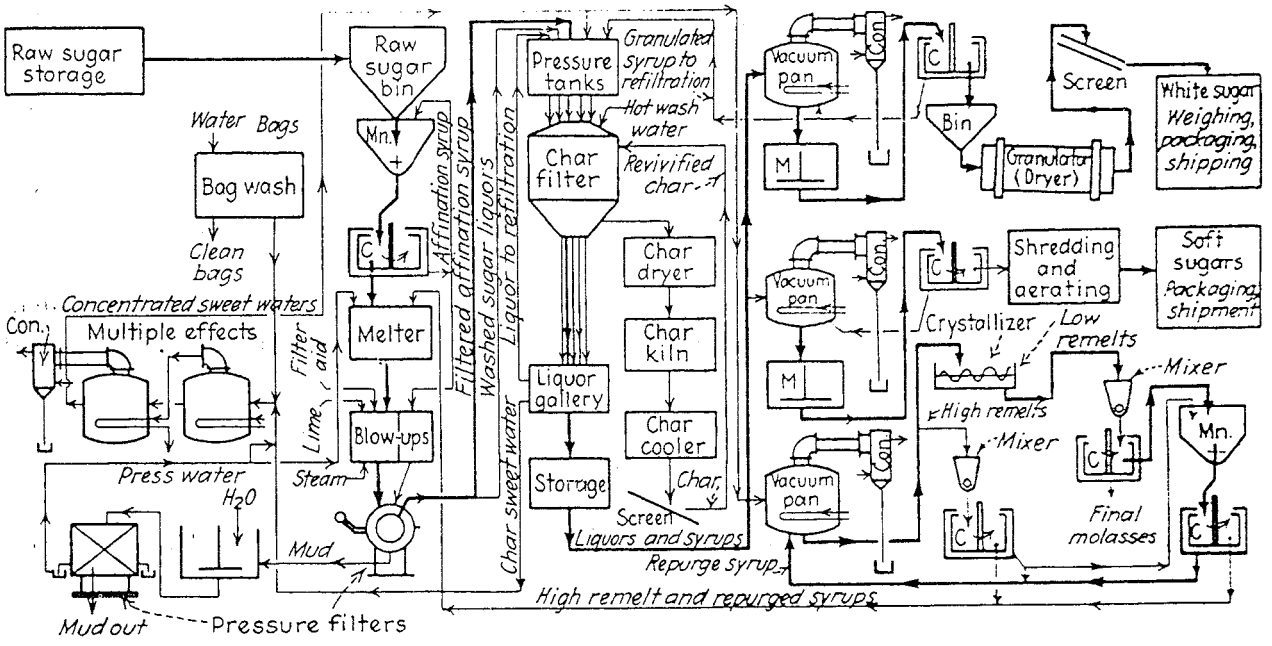
[6]For vacuum evaporation equipment and accessories, heat-transfer data, and condenser water data, see Perry, pp. 11-28 to 11-38.

[7]Birch and Parker, op. cit.; Labine, Melt House Redesigned for Automatic Flow, *Chem. Eng.* 67 (9) 94 (1960); ECT, 2d ed., vol. 19, 1967, p. 185.

[8]The degree Brix is the percentage, by weight, of sucrose in a pure sugar solution; commercially it is taken as the approximate percentage of solid matter dissolved in a liquid.



In order to produce 100 kg of refined sugar (about 400 kg residual syrup is also produced), the following materials and utilities are required:

Raw sugar (97°Pol.)	106 kg	Condensing water	2000–3500 kg
Hydrated lime	0.05 kg	Pure water	600 kg
Kieselguhr	0.25 kg	Power process steam	175 kg
Bone char (in process)	105–250 kg	Power steam	
Bone char (revivified)	35–75 kg	Char kiln fuel	58 MJ
Bone char (new)	0.25–0.3 kg	Direct labor	0.66 work-h

Fig. 30.2. Flowchart for refined cane-sugar manufacture. KEY: Mn, mingler; M, mixer; Con, condenser; C, centrifugal.

The resulting syrup is removed by a centrifuge, and the sugar cake is sprayed with water. The crystals are dumped into the melter, where they are dissolved in about half their weight of hot water, part of which is sweet water from the filter presses. The syrup from the centrifugals is divided, part being diluted and reused as mingler syrup and the remainder diluted to about 54° Brix and sent either to the char house for clarification and refiltration or to the pans to be boiled with remelt.

The melted and washed raw sugar (in refineries, melted means dissolved) is then treated by a process known as clarification or defecation. Either mechanical or chemical processes can be used. Mechanical clarification requires the addition of diatomaceous earth or a similar inert material; the pH is then adjusted and the mixture filtered in a press. This system gives an absolutely clear solution of slightly improved color and is inherently a batch process.

The chemical system uses either a frothing clarifier or a carbonation system. Liquor treated for frothing, containing entrapped air bubbles, enters the clarifier at about 65°C. In the clarifier it is heated, causing a froth to form which rises to the surface carrying gelatinous tricalcium phosphate and entrapped impurities. The clarified liquor is filtered and sent to decolorization. This process reduces the coloring matter present by 25 to 45 percent, which greatly reduces the size of the subsequent decolorizers.

The carbonation system adds carbon dioxide from scrubbed flue gas to the melted sugar, which precipitates calcium carbonate. The precipitate carries down with it over 60 percent of the coloring matter present and is removed by filtration.

DECOLORIZATION-CHAR FILTRATION. The clarified effluent liquor, now free of insoluble material, still retains a large amount of dissolved impurities. These impurities are removed by percolation through bone char.[9] (Activated carbon is also used.) The char tanks are about 3 m in diameter and 6 m deep. From 20 to 80 char filters are required per 1×10^6 kg of melt. The percolation is carried out at about 82°C, and the initial product is a clear, water-white syrup. Experience teaches the operator when to shift the char-filter effluent to a lower grade of syrup.

After a certain amount of use, the char loses its decolorizing ability and must be revivified. This is done approximately every hour by first washing it free of sugar, removing it, and roasting it. A continuous decolorizing process is also used.

The syrups from the bone-char filters are piped to the liquor gallery, where they are graded according to purity and strength: 99- to 99.7-deg purity, 90- to 93-deg purity, 84- to 87-deg purity, and 75- to 80-deg purity.

Darker-colored liquors are treated with either bone char, synthetic bone char (Synthad), activated carbon, ion-exchange resins, or some combination to form what are known as "soft brown sugars." When the bone char loses its decolorizing power, it can be revivified by heating it to 400 to 500°C in vertical pipe or Herreschoff kilns. Careful heating ensures that the active surface is not oxidized away.

Activated carbon is superior to bone char as a decolorizer because its adsorption cycle is longer, but it does not remove inorganics. Coarse carbon granules can be used in beds like bone char and revivified by roasting at a higher temperature (1000°C). For small installations or seasonal batches, once-through decolorization employs powdered carbon, which is discarded after a single use. A recent development makes use of a decolorizing chemical additive, dioctadecyl dimethylammonium chloride (Talofloc) and a proprietary flocculating agent of polyacrylamide (Taloflote). It has been reported[9] that clarity and capacity can be increased by 75 percent by such a system. Where inorganic salts are a problem, ion exchange can be used to remove them. A cation exchanger absorbs cations from solution leaving it very acid.

An anion exchanger (usually mixed with the cation exchanger) then removes the free acid. The combination does an excellent polishing job. Ion exchange has been extensively tested[10] as a complete replacement for char/activated carbon treatment but has cost too much. The major problems are fouling of the resin and handling the wash waters used during the regeneration for reuse.

Figure 30.3 shows a cross section of the crystallizing, or "strike," vacuum pan. Here the sugar syrup is concentrated to a predetermined degree of supersaturation; when it is seeded with a measured amount of fine sugar. These small crystals are grown to a marketable size by a properly regulated rate of boiling or evaporation, as well as of agitation and syrup inflow. The rate should not be too rapid, or new crystals (false grains) will be formed and not have time to grow, with consequent loss through the screen of the centrifuge.

The purest syrups are reserved for liquid sugar (water-white), the next purest for tablets and granulated sugar, and the remainder goes to canners and bottlers, confectioners, and soft sugars (brown).

The pan is discharged into a mixer, which keeps the whole mass from sticking together, and is then sent to centrifuges, where the crystals are separated from the syrup, washed, and dropped to the wet-sugar storage bin.

The syrup is returned to the process for further recovery of sugar.

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[9]Jones and Lopez, Sugar, *Ind. Technol.* 35 22 (1976).

[10]ECT, 3d ed., vol. 13, 1980, p. 703.

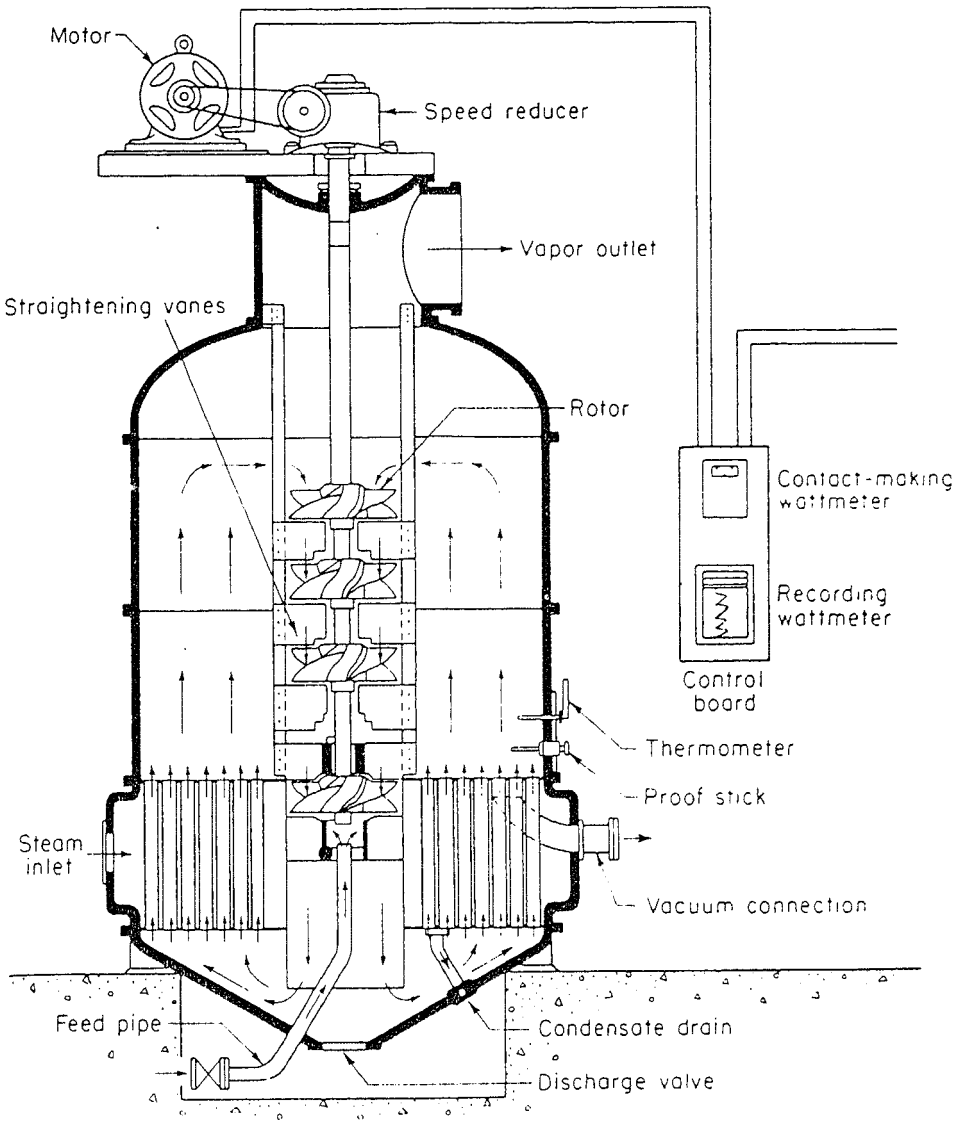

Fig. 30.3. Cross section of vacuum pan with mechanical circulator. The syrup is heated by passage upward through the tubes of the steam chest, or *calandria*, near the bottom. The liquid boils at the upper surface, and vapor is drawn out through the large central pipe. A set of screw impellers forces the liquid back through the central downtake pipe. The stirrer is motor-driven and has recording and controlling watt meters in its circuit. (*Esterline-Angus Co.*)

When the purity of the syrup becomes too low, it is used for blended table syrups, the poorer lots going for animal feed. This syrup is commonly called molasses or blackstrap.

The wet sugar is dried in a granulator, which is a horizontal rotating drum about 2 m in diameter and 8 m long having a series of narrow shelves (flights) attached to its inner surface. These flights lift the sugar and allow it to fall through the stream of hot air flowing countercurrent to it.

The dried crystals pass over a series of screens, where they are graded according to size.

Various automatic packing and weighing machines put up the sugar in bags and boxes with a growing percentage in bulk.

Powdered sugars are made by grinding granulated sugar in mills but are so hygroscopic that mixing with 3% corn starch is practiced to make confectionery grades. Cube and tablet sugars are prepared by mixing certain types of granulated sugar with a heavy white syrup to form a moist mass, which is then molded and dried.

The yield of refined sugar obtained, based on raw sugar of 96° polarization, is usually 95 to 94 percent, syrup 5 percent, and mechanical and wash losses 0.7 percent

In handling sugar, some inversion takes place according to the following reaction

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{d\text{-Glucose}}{C_6H_{12}O_6} + \underset{d\text{-Fructose}}{C_6H_{12}O_6}$$

Polarization	+66.6°	+52.8°	−92.8°

The product is called *invert sugar*, but the polarization of the pure sucrose of +66.6° (+ to the right) now reads −20.0° (− to the left) for the resulting mixture

$$\frac{+52.8° - 92.8°}{2} = -20.0°$$

The continuous adsorption process used by The American Sugar Refining Co.[11] at its Bunker Hill refinery, using *bone char continuously*, is a fundamental improvement in the purification process used for decades. Here, in decolorizing columns 4 m in diameter, with 12-m beds of bone-char adsorbent, the sugar liquor moves upward at a uniform rate controlled by the results desired, and the bone char moves downward, though at a slower rate than that of the syrup. The particles of bone char are slightly separated, or "expanded," resulting in maximum and uniform adsorption of impurities from the sugar liquor in a truly countercurrent continuous flow; the bone char of the highest adsorptive capacity is automatically in contact with the sugar liquor of the lowest level of impurities. This results in a more efficient use of the bone char, with no sugar liquid blending and no liquor gallery. Also, the color of the product liquor can be adjusted by simply adjusting the feed rate of the bone-char in relation to that of the sugar liquor. High-quality granulated sugar has been produced using "no more than 10 to 15 kg of bone char per 100 kg melt"—much less than normally used. The bone char is degraded in only a minor way, if at all. Finally, it is claimed that the capital required for this step has been halved and the labor reduced 90 percent together with other savings. The spent char is desweetened, deashed in columns, dewatered to 20% moisture or less, and reactivated in a low-oxygen (1–2% O_2) atmosphere continuously, in a multiple-hearth kiln

BAGASSE. The burning of about 70 percent of the bagasse produced furnishes enough steam for power heat to run the mill. Hence 30 percent is available to make an insulating and building board like Celotex or to digest the bagasse with chemicals (NaOH, etc.) to a pulp for paper manufacture on Fourdrinier machines. Furthermore, often much more than the 30 percent is used for such by-products when other fuel is available at a cheaper price than the $5 per ton traditionally assigned to bagasse. The amount of bagasse usually available is equal to the sugar yield

The bagasse is conveyed by an endless belt to the rotary digesters, which are 4.3 m in diameter, and is cooked under pressure in order to render the fibers pliable, loosen the encrusting material, dissolve organic material, and sterilize the fiber. The resulting pulp, in a 2 to 3% suspension, is pumped to swing-hammer shredders and washed in specially designed rotary washers in order to remove dirt, soluble compounds, and some pith. From the washers, the pulp enters half stock chests, where the sizing, usually papermakers' rosin and alum, is

[11] U.S. Patent 2,594,305, September 27, 1960; Marev (American Sugar Refining Co.), "Adsorption by Bone Char Using Continuous Absorption Process," 20th Annual Meeting of Sugar Industry Technicians, New York, May 1981.

added and the mass stirred with powerful agitators to remove any irregularities. The fibers are refined in conical refiners to give optimum fiber size. The refined fiber goes to stock chests, from which it is fed, as an approximately 2% suspension, to the head box of the board machine. In the head box it is diluted to about 0.5%. The board machines, although of special design, are similar to Fourdrinier machines. The stock is fed onto forming screens and led to drying felts and finally to press rolls. The sheets do not appear laminated but are felted together to give the required thickness. The board from these machines is 4 m wide, contains 50 to 55% water, and is produced at the rate of 60 m/min. It is dried in a continuous sheet, at 150 to 230°C in a gas- or steam-heated dryer 250 to 300 m long. The product must be sprayed with water as it leaves the dryer in order to bring it up to its normal water content of approximately 8%. The board is then cut and fabricated.

Acoustical and structural wallboard, agricultural mulch and litter, plastic filler, furfural, paper and plastic reinforcing fibers have all been made from bagasse. A high-quality wax has also been extracted.

BEET SUGAR. Cane grows well only in tropical and semitropical climates, but sugar beets grow well in the temperate zones. Only a skilled chemist can tell whether a sample of refined sugar originated from the cane or the beet. Sucrose content of both sugars is very high, over 99.9%. For all normal purposes, the sugars obtained are interchangeable. All plants produce some sugar, but only beets and cane are major sources. Other minor sources are the maple tree, certain palm trees, and honey. Food value and sweetness (but not sucrose) are economically obtained from corn, which increasingly effectively competes with beets and cane. Corn seems to be gradually diminishing the beet market in the United States.

The sugar beet differs from the ordinary table beet in that it is much larger and is not red. Sugar beets are an important crop in many sections of the world because of their sugar value.

Beet houses begin operation in late September and run until January or February, the farmer harvesting the crop with machines that uproot the beets and elevate them to trucks. The tops, good for cattle feed, may also be removed mechanically. The beets, containing from 13 to 17% sucrose and 0.8% ash, enter the factory by way of flumes, small canals filled with warm water, which not only transport them but wash them as well.

Figure 30.4 illustrates the essential steps in the making of beet sugar. This manufacture may be divided into the following sequences:[12]

The beets are rewashed, weighed, and sliced into long narrow strips called cossettes.

The cossettes are dropped into a specially designed continuous countercurrent diffuser (Fig. 30.4). The sugar is extracted countercurrently with water at 70 to 80°C. The resulting raw juice is a blue-black 10 to 12% sucrose solution with a small amount of invert sugar and 2 to 3% ash. The pulp remaining contains 0.1 to 0.3% sugar (based on the beets). The pulp is dewatered in presses, dried in a rotary dryer, and sold as cattle feed. The change in the beet industry to automatic countercurrent continuous diffusers eliminates the sweet-water handling costs and reduces the labor required by the battery.[13] The amount of energy consumed is sharply reduced.

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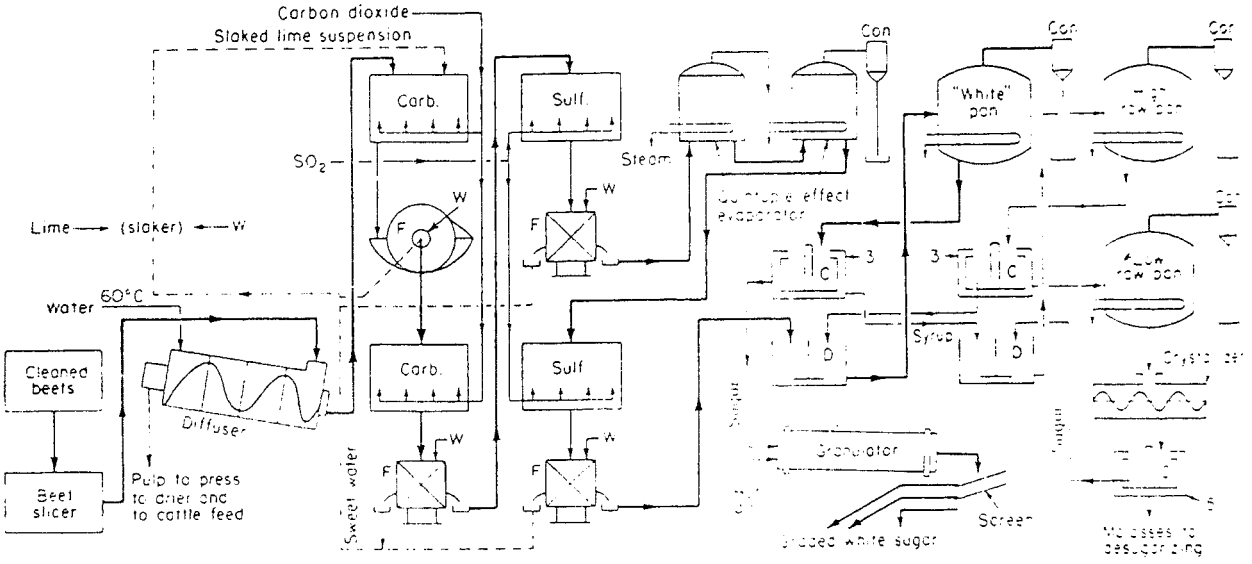
[12]See also pictured flowchart, Beet Sugar Production, *Chem. Met. Eng.* 49 (6), 110 (1942); McDill, Beet Sugar Industry; Industrial Wastes. *Ind. Eng. Chem.*, 39 657 (1947); Birch and Parker, op. cit.

[13]Havighorst, Beet Sugar: A Radical New Look, *Chem. Eng.* 68 (20) 76 (1961); Spreckles' New Developments in Beet Sugar, Part 1, *Chem. Eng.* 71 (7) (1964).



In order to produce 1 t of refined sugar, 400 kg molasses (50% sucrose), and 400 kg dried pulp, the following materials and utilities are required:

Farm land	0.2 ha	Coal (power and heating)	0.66 t
Sugar beets	8 t	Sulfur	0.5 kg
Limestone	0.35 t	Water	9.0 t
Coke	0.03 t	Direct labor	2.2 work-h

Fig. 30.4. Flowchart for beet-sugar manufacture. KEY: Carb, carbonators; sulf, sulfitors; F, filters; W, wash water; C, centrifugals; Con, condensers; D, dissolvers. NOTE: About half of all plants use sweet water from filter washing for slaking lime; others use fresh water.

The juice is given a rough screening to remove foreign materials.

Milk of lime is added until the concentration is equivalent to about 2 to 3%. The lime aids in the precipitation of undesirable impurities. Any calcium saccharate is decomposed in carbonators by passing carbon dioxide from the lime kiln through the juice continuously. The foaming that occurs at this stage is reduced by adding a small quantity of antifoam.

The sludge produced by the lime is equal to 4 or 5 percent of the weight of the beet charged. This is removed by thickening and filtering on rotary filters.

Lime is added again until the concentration is equivalent to 0.5 percent and the juice again carbonated, this time hot.

It is then filtered on pressure filters.

The resulting filtrate is bleached with sulfur dioxide.

The precipitate of calcium sulfite is removed by pressure of plate-and-frame filters.

The purified juice is concentrated from 10 to 12% sugar to about 60% sugar in multiple effect evaporators. This increases the concentration of calcium ions again. Some calcium precipitates out.

A Spreckles' plant uses also a countercurrent decolorizing reactivated carbon adsorption system to purify and decolorize the thick juice in towers, where the juice rises against the falling carbon.

The resulting thick juice is grained in vacuum pans,[14] centrifuged, washed, dried in a granulator, screened, and packed in much the same manner as described for cane sugar.

[14]McGinnis et al., Low-Purity Beet Sugar Factory Materials, *Ind. Eng. Chem.* 34 17 (1942).

The juice from the first vacuum pan is given further treatment to recover more sugar crystals, but this is not pure enough for market and is sent back to the process for further purification.

The syrup remaining after the several crystallizations, called beet molasses, is sold for cattle feed directly or added to the waste beet pulp. It is also an important medium for fermentation, particularly for citric acid, where the high nitrogen content of beet molasses is favorable. Processes for recovery of the remaining sugar have been worked out and are used commercially. Initial recovery was obtained by the Steffen process, which is used extensively in the United States.

Diluted molasses yields up its sucrose by precipitation as a metal saccharate; impurities are removed from the precipitate by filtration; the sucrose is then regenerated. Calcium, strontium, or barium each form insoluble saccharates with sucrose, but the calcium process is generally preferred. The process using $Ca(OH)_2$ as the precipitant is known as the Steffen process, after its inventor. Regeneration of the calcium saccharate results from treating the material with CO_2 and approximately 90 percent of the sucrose can be recovered by the Steffens process. The $CaCO_3$ precipitated can be roasted and reconverted to milk of lime.

Ion exchange[15] has been tried or proposed for the treatment of process liquors at several places in the sugar-manufacturing procedure. Ion exchange works well for cleaning up process liquors, but total-output treatment is frequently too expensive because of the cost of disposal of sweet waters and spent reagents (from washing). Resin life is also short because of irreversible absorption. With cane sugar inversion may take place and cause losses.

In cases where inversion is desired, ion-exchange offers a good, controllable method.

Liquid-phase chromatography[16] is being utilized in a commercial plant to separate sucrose from beet molasses, but the process is too new to evaluate its commercial possibilities.

ENERGY REQUIREMENTS. In the direct manufacture of sugar there are few or no chemical changes that require energy. Almost all the steps in the manufacturing sequences involve physical changes or unit operations. These consume energy in the form of power for crushing, pumping, and centrifugation and heat for solution, evaporation, and drying. At the bottom of the flowcharts for refined cane sugar and for beet sugar (Figs. 30.2 and 30.4) some average figures for energy requirements are given. The steady improvement of the equipment necessary to make these various unit operations function efficiently has gradually reduced the energy requirements to the reasonable amounts given, but much remains to be done.

Although bagasse is used for fuel in many raw-sugar mills, it is becoming a more important raw material yearly for paper and board; hence other fuel may be employed. In all sugar-manufacturing establishments, there is an economical dual use of steam possible (see Table 4.5) wherein high-pressure steam from the boiler is expanded through a turbine to furnish power and the exhaust steam is condensed to secure heat for evaporation of the juices and syrups. The condensate water resulting is pumped back to the boilers or employed in making syrups. For beet-sugar refining, Fig. 30.4 indicates 0.66 t of coal for 1 t of refined sugar, or 28.2 MJ per kilogram of sugar. Some plants now produce 1 kg of refined beet sugar with under 13.9 MJ.

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[15]Michener et al., Ion Exchange in Beet Sugar Factories, *Ind. Eng. Chem.* **42** 543 (1950). Mandru, Ion Exchange in Beet Sugar Manufacture, *Ind. Eng. Chem.* 43 615 (1951).

[16]Heikkila, Separating Sugars and Amino Acids with Chromatography, *Chem. Eng.* 90 (2) 50 (1983).

MISCELLANEOUS SUGARS. Lactose, or milk sugar, is made from waste skim milk. Sorbitol is manufactured by hydrogenation of dextrose under pressure, using a nickel catalyst, or by reduction in an electrolytic cell. *Mannitol,* made by hydrogenating sucrose to yield a 3:1 sorbitol/mannitol mixture difficult to separate, is used in pill manufacture and electrolytic condensers. *Xylitol,* a sugar alcohol made by reduction of xylose, is now produced on a large scale. It can be assimilated by diabetics without use of insulin, is nonfermentable, and does not promote dental caries, so it is used in high-priced dietetic candies, chewing gum, toothpastes, etc. *Gluconic acid,* made by oxidizing glucose by fermentation or by electrolytic oxidation, forms useful calcium and iron salts used pharmaceutically.

CORN SWEETENERS. A major portion of nutritive sweeteners now comes from starch (mainly corn) conversion into fructose-containing syrups. Conversion of starch into glucose by treatment with acid or with the enzyme α-amylase has been practiced for many years, and the syrups thus obtained are nourishing but not very sweet tasting. The discovery that enzymes could be immobilized on organic substrates such as diethyl-aminoethyl cellulose or certain ceramic materials made enzyme use economically possible because a single charge could serve for a comparatively long period (several hundred hours) and treat a considerable quantity of material before requiring replacement. Glucose syrup prepared from starch by treatment with α-amylase can be treated with a different immobilized enzyme, glucose isomerase (see Fig. 30.5), which can convert up to 42 percent of the glucose to fructose, which has 1.3 times the sweetening power of sucrose. This syrup can be used directly as a sweetening syrup essentially equivalent to sucrose syrup or, by separating fructose and recirculating the syrup over the enzyme, 55% fructose can be made. This material can be dried, but because the solid formed is hygroscopic, it is not very desirable for home use. In 1980, 42% syrup sold for 64 cents per kilogram, 55% for 75 cents per kilogram, and refined sugar for 81 cents per kilogram, in comparable bulk quantities.

Another procedure can be used to make 95 to 100% fructose. This passes the glucose solution over a bed of immobilized glucose-2-oxidase, which oxidizes the glucose to glucosone, which can in turn be hydrogenated to fructose.[17] The process is not yet commercial.

[17]Basta, Immobilization Routes, They're Not Standing Still, *Chem. Eng.* 89 (17) 55 (1982).

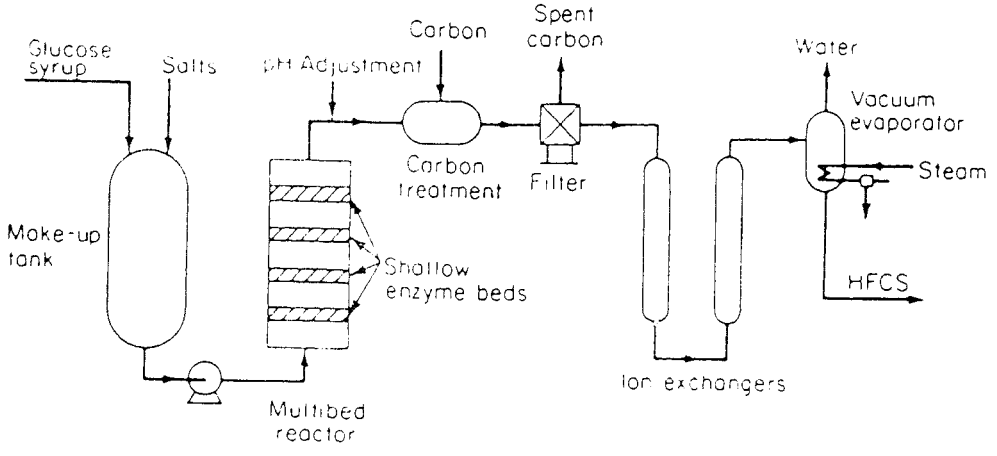
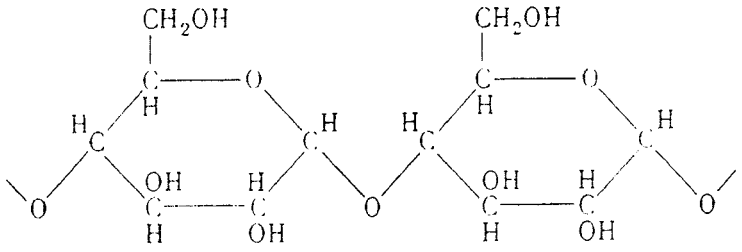


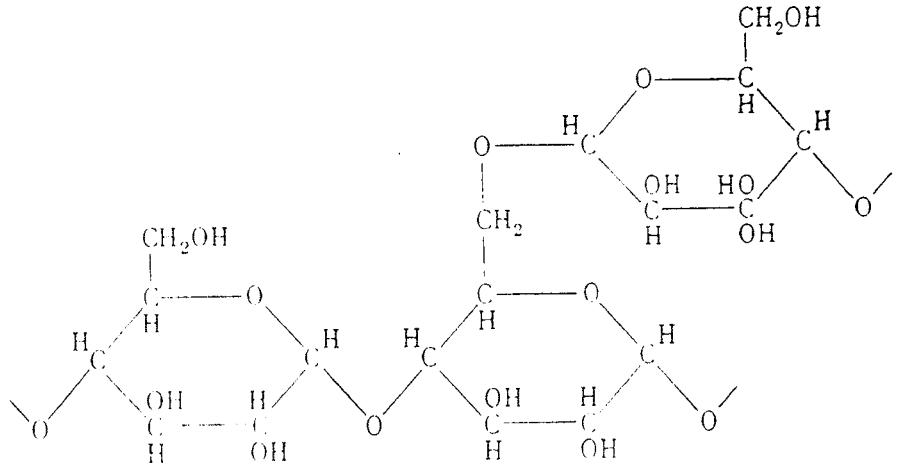
Fig. 30.5. Fructose/glucose syrup from glucose syrup.

STARCHES AND RELATED PRODUCTS

Starch consists of a chain of D-glucopyranosyl units and has the general formula $(C_6H_{10}O_5)_n$ with n = 250 to over 1000. Two major components are recognized as usual, a branched-chain form, amylopectin (75 to 80% in common starches), and a linear form, amylose.



Amylose: segment of a linear chain



Amylopectin: segment of a branched chain

Starch is one of the most common substances existing in nature and is the major basic constituent of the average diet. Industrially, its applications[18] are numerous, and it is used in more than 300 modern industries, including the manufacture of textiles, paper, adhesives, insecticides, paints, soaps, explosives, and such derivatives as dextrins, nitrostarch, and corn sugar. In recent years such derivatives as heat-resistant adhesives, esters comparable with cellulose esters, carboxylic acids from the oxidation of dextrose, and wetting agents have been produced.

HISTORICAL.[19] It is a well-known fact that the ancients used starch in manufacturing paper (as an adhesive and stiffener) as early as 3500 B.C. The Egyptians of this period cemented papyrus together in this manner. Between A.D. 700 and 1300, most paper was heavily coated with starch, but the practice was abandoned toward the end of the fourteenth century and was not revived until the modern era. The use of starch in textiles began during the Middle

[18]The Corn Industries Research Foundation, Inc., 1001 Connecticut Ave., Washington D.C., publishes an important series of pamphlets on the corn wet-grinding industries, which are kept up to date. Titles are *Corn in Industry, Corn Starch, Corn Gluten, Corn Act, Corn Syrups and Sugars.*

[19]Knight, *The Starch Industry*, Pergamon, Oxford, 1969.

Ages, when it was a common stiffening agent. By 1744 the English were using it in sizing and warp glazing. Textile demands soon brought about the introduction of potato starch to supplement the wheat starch solely available up to this time. In 1811 the discoveries of Kirchhoff with respect to glucose and the thinning of starches by enzymic action gave great impetus to starch manufacture through the increased fields of application created. The use of roasted starch (dextrins) did not begin until 1821, its usefulness being discovered as the result of a textile fire at Dublin, Ireland. It had, however, been prepared by LeGrange as early as 1804. The first starch produced in this country was white potato starch, made at Antrim, N.H., in 1831. In 1842, Kingsford began the production of cornstarch, which became increasingly popular until, by 1885, it had risen to the position of the leading textile starch in the field. It was in this period also that the manufacture of dextrins (roasted starches) began in the United States.

USES AND ECONOMICS. In 1981 about 6.7×10^9 kg of starch was produced in the United States for all purposes, including conversion into syrup and sugar. Of this total about 98 percent was cornstarch. Imports are principally tapioca, sago, and arrowroot starches, and exports are principally cornstarch. The largest single use for cornstarch is as food, about 25 percent being thus consumed. Industrial uses account for the remaining 75 percent. The paper industry utilizes cornstarch as a filler and a sizing material. Textile, laundry, foundry, air flotation, oil-well drilling, and adhesives use much starch (Chap. 25). White potato starch can be employed for almost every one of the uses outlined for cornstarch; it has a more desirable phosphoric acid content but is more expensive.

Wheat, rice, arrowroot, and cassava (tapioca) starches also have many of the same applications as cornstarch. Rice starch is particularly preferred for laundry purposes. Tapioca starch is very common as a food. In addition to the starches themselves, many further reaction products are made. These include the following products: dextrin, which is available in more than 100 different blends and types varying from pure white to light yellow in color is used to make a great number of different pastes, gums, and adhesives. Corn syrups are a hydrolysis product of cornstarch, containing dextrose, maltose, higher saccharides, and water. Approximately 95 percent is used for food, and varying types are offered to the trade: conventional syrups, primarily dextrose made by acid or enzyme hydrolysis; syrup solids and crystalline dextrose made by drying conventional syrup; and three grades of high-fructose corn syrup (HFCS) made by conversion with a special enzyme and containing 42%, 55%, and 90% fructose. Nonfood and industrial applications are important, as in the textile, leather-tanning, adhesive, pharmaceutical, paper, and tobacco industries. Corn sugar, or dextrose, is the sugar found in the blood and is our primary energy food. Its many food uses are dependent upon its lower rate of crystallization, lesser sweetness, and different crystal formation. Dextrose is consumed in baking and has additional uses in preserved foods, soft drinks, candy, and ice cream. It is widely employed by the medical profession for infant feeding and for prescriptions in syrup form. Industrially, it is important as a constituent of the viscose-rayon spinning bath, in leather tanning, in tobacco conditioning, and in fermentation. Important by-products of the starch industry are corn gluten, feed and meal, corn-oil meal, and corn oil. Virtually all gluten and meal are used as feed, but a specially prepared gluten, very high in protein, is employed as a raw material in manufacturing plastics and lacquers. Concentrated steep water is consumed in the growing of penicillin and streptomycin (Chap. 40). Inositol, or hexahydroxycyclohexane, a sugar substance and a member of the vitamin B complex, is made from corn steep water.

MANUFACTURE OF STARCH, DEXTRIN, AND DEXTROSE FROM CORN. Corn wet refining is a large industry, processing more than 12.8×10^9 kg of corn per year. Chemically, the corn kernel consists of from 11 to 20% water, with the following average constituents, expressed in percent.[20]

Moisture	16	Oil	3.8
Starch	61	Fiber	2
Proteins	9	Sugars	1.6
Pentosans	5.3	Ash	1.3

On this basis, 100 kg of corn yields 51.3 kg of starch, 39.2 kg of by-products (gluten meal, corn bran, germ-oil meal, and steep water), and 2.8 kg of corn oil.

The refining process utilizes wet milling in a dilute sulfurous acid medium using shelled corn as the raw material,[21] as shown in Fig. 30.6. The sequences are as follows:

The first operation consists of cleaning the corn by means of screens, compressed air, and electromagnets. The cleaned corn is soaked (steeped) for 2 days in circulating warm water (46 to 52°C) containing 0.10 to 0.30% sulfur dioxide to prevent fermentation during the soaking period. Large hopper-bottomed wood or stainless-steel steeping vats (holding 8200 kg of

[20]Corn Industries Research Foundation, op. cit., 1958.

[21]Forbath, Process Maze Yields Maize Products, *Chem. Eng.* 68 (5) 90 (1961) (flowchart); Wet Milling of Corn, *Chem. Eng.* 69 (16) 117 (1962).

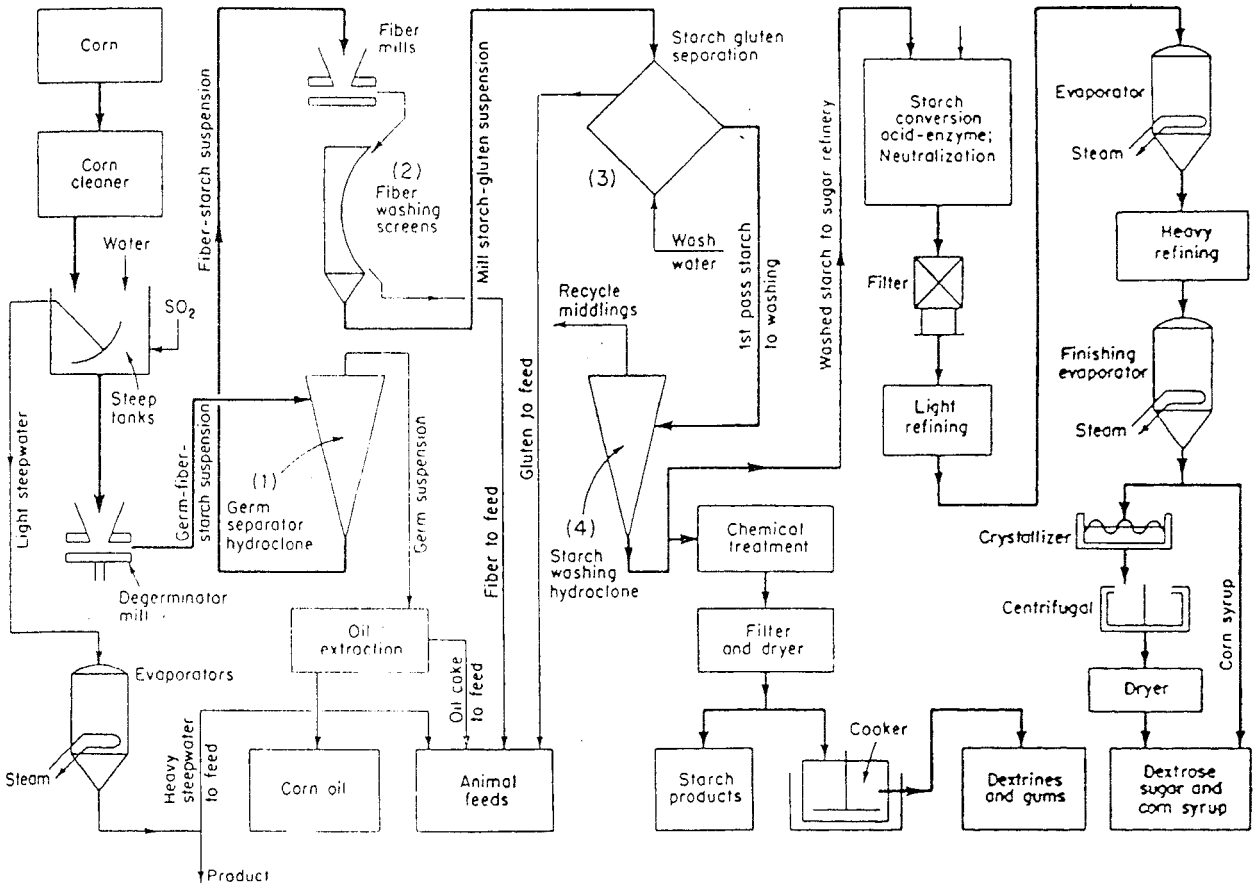


Fig. 30.6. Corn products outline flowchart. *(Corn Products Refining Corp. and Dorr-Oliver.)*

corn) are employed for this operation, which softens the gluten and loosens the hulls. The steep water dissolves salts, soluble carbohydrates, and protein.

The cleaned and softened kernels are degerminated between two studded steel plates, one rotating and one stationary, which tear the kernels apart and extricate the corn germs without crushing them. The corn germs are liquid-separated from the hulls in so-called *germ separators*, formerly large, agitated tanks. Now stationary cone-shaped hydroclones[22] (Fig. 30.7) are more efficient, using continuous gravity separation of the germ by the centrifugal action of a tangentially injected suspension of germ-fiber starch, with the lighter germ in the overflow (top center). This results in a cleaner and more accurate process at less capital investment. The germ is subjected to oil extraction as described in Chap. 28, using either expellers or solvent extraction.

The remainder of the corn kernel contains starch, gluten, and cellulosic fiber. It is wet-ground in impact fiber mills and passed through high-capacity stationary screens[23] called sieve bends, depicted in Fig. 30.8. In the sieve bends the starch and gluten are washed countercurrently with process water to remove them from the fiber, which is the oversized material, all of which was mechanically separated in the fiber-milling operation.

To separate the heavier starch from the gluten, the old, cumbersome, gravity starch tables

[22]Dorr-Oliver, Hydrocyclones, *Chem. Eng.* 71 (1) 48 (1964).

[23]Elsken and Ehenger, Stationary Screens, *Chem. Eng. Prog.* 59 (1) 76 (1963).

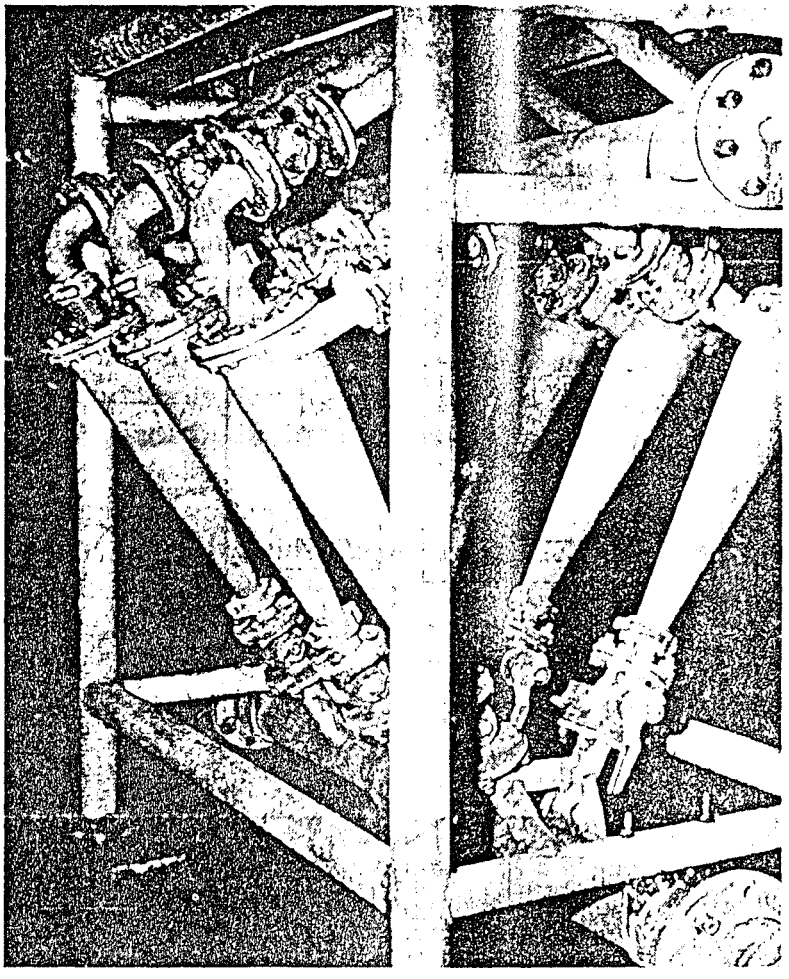


Fig. 30.7. Germ-separating 15.2-cm-diameter hydroclones. All six hydroclones shown operate in parallel with the lighter germ in the central overflows. *(Dorr-Oliver.)*

Fig. 30.8. Fiber-washing 120° sieve bend. Stationary screens of a 120° arc. *(Dorr-Oliver.)*

have been discarded, and this separation is now done in pressure-nozzle discharge centrifuges (Fig. 30.9) and purification by pumping through starch-washing hydroclones[24] (Figs. 30.10 and 30.11) from which the "middlings" are returned to the centrifuge for recycling. These centrifugal devices intensify the force of gravity, require less space, and are cleaner, since they are completely enclosed. The gluten, as shown in Fig. 30.6, is sent to be mixed with oil cake and fiber for animal feed. Some gluten is partially dehydrated and sold as an adhesive or alcohol-extracted to yield zein.

The highly mechanically purified starch is dried and sold or "cooked" to heat-convert it to soluble dextrins and gums.

Over 70 percent of the cornstarch produced by wet milling is now used in the manufacture of corn sweeteners, principally HFCS. A modest percentage of the syrup formed is converted to crystalline dextrose using crystallizers similar to the one shown in Fig. 30.12.

If *commercial starch* is to be made, the starch is removed from suspension with a vacuum rotary string-discharge filter. The cake is broken and dried by flashing or in a continuous-tunnel dryer traveling countercurrent to the air. The starch enters with a moisture content of 44% and exits at 10 to 14%. This form is sold as *pearl starch*. Powdered starch is ground and

[24]James, *Industrial Starches*, Noyes, Park Ridge, N.J., 1974; Bradley *The Hydroclone*, Pergamon, Oxford, 1965.

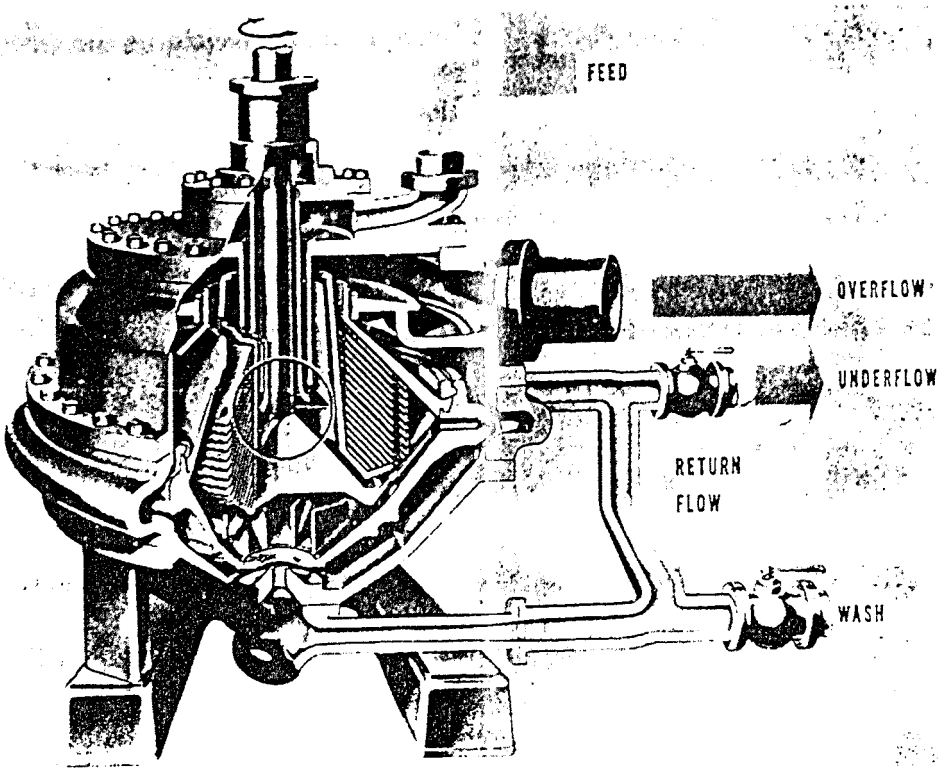


Fig. 30.9. Gluten separation (overflow) by a Merco disk pressure-nozzle bowl centrifuge. The suspension enters into the center feed well, at the bottom of which the impeller throws the slurry to the outer portion of the disk stack. Here centrifugal force throws the heavier starch toward the periphery of the rotor and, as a result, the starch particles settle on the underside of the individual disks and slide down to the outer area of the bowl, where the concentrated starch slurry is discharged through the nozzles (on the periphery) and through the underflow. A somewhat similar Merco centrifuge is used to thicken the separated gluten-water fraction.

screened pearl starch. *Lump*, or *gloss*, *starch* is made from powdered starch containing a slightly higher percent of moisture. Precooking the starch yields *gelatinized starches*. For *thick-boiling starch*, alkali conversion is used; for *thin-boiling starch*, mild acid conversion. Oxidized starch, also known as *dialdehyde starch*, is made by treating starch with hypochlorite or electrolytically produced periodic acid. Specialized food starches known as *cross-linked starches* result from treatment of starch with $POCl_3$, epichlorohydrin, or sodium metaphosphate. *Starch esters* such as *starch acetate* and ethers made with ethylene or propylene oxide enjoy considerable use as textile sizes.

Another product of corn refining is *dextrin*, or roasted starch. Starch itself is not soluble in water, but its derivative, dextrin, dissolves readily to give various commercial adhesives, pastes, and gums. Conversion is carried on in round, steam-jacketed tanks equipped with a scraper and open at the top. The scraper prevents sticking during the heating period, which may vary from 2 h for some white dextrins to 15 h for certain gums. The temperature also influences the kind of dextrin being prepared.

The average yield of sugar from a hectare of cane is 13,400 kg. A hectare of beets usually produces about 8400 kg of sugar. Present corn yields approach 13,600 kg of grain per hectare. The 13,600 kg of corn grain will produce 9700 kg of starch which can be converted to 10,100 kg of glucose. Since cane requires about 18 months to produce and corn less than half that, it is apparent that, if acceptable sweeteners can be made from cornstarch, yields per hectare-year are far greater and costs consequently less than for cane even if the value of corn oil,

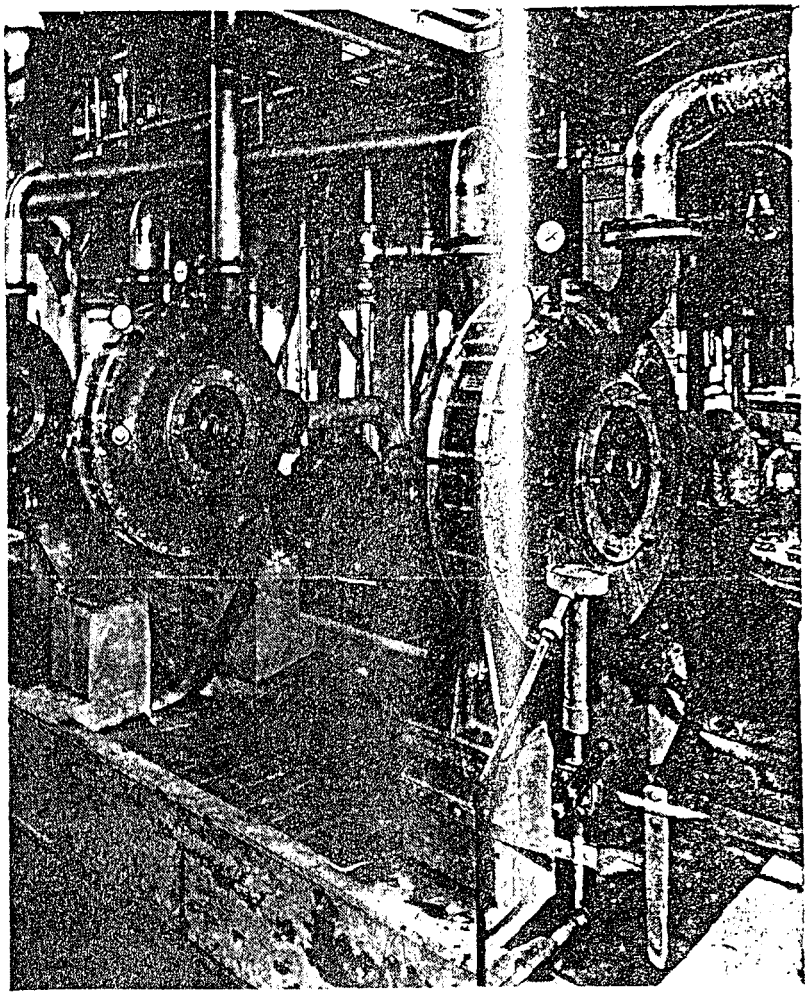


Fig. 30.10. Purification of starch through gravity accentuated by centrifugal washing in multiple hydroclones. These hydroclones are much different than those of Fig. 30.7, being only 10 mm in diameter and made of nylon, with up to 480 arranged in a separate housing, and operating in parallel. By employing a series of nine of these multiple hydroclone units, both insoluble protein (gluten) and solubles are removed from the starch slurry. *(Dorr-Oliver.)*

protein, and ensilage is ignored. This favorable economic situation has led to the conversion of over 70 percent of the cornstarch produced to sweetener for food use.[25]

A variety of other products and by-products from starch processing are commercially important. Many starch-containing adhesives have become important.[26] Superabsorbents capable of absorbing up to 1500 times their weight of water[27] are starch graft polymers using polyacrylonitrile as the cross-linking agent. Basic caramel is made by starch modification. The

[25]Starch as a Source of Sweeteners, *Die Starke* November 7, 1973, p. 1; Wieland, *Enzymes in Food Processing and Products*, Noyes, Park Ridge, N.J., 1972; Rosenzweig, A Sweet Future Buoys High-Fructose Corn Syrup, *Chem. Eng.* 83 (20) 54 (1976); Vulleumier, Corn Sweeteners Outlook, *Sugar J.* 43 (8) 13 (1981).

[26]Ziegler and Adams, *Survey of the Literature on Starch Adhesives*, Washington State University, Pullman, Wash., 1970.

[27]Worthy, Super-Slurper Gaining Commercial Application, *Chem. Eng. News* 57 (45) 23 (1979); Superabsorbents Seek Markets That Are Super, *Chem. Week* 125 (3) 40 (1979).

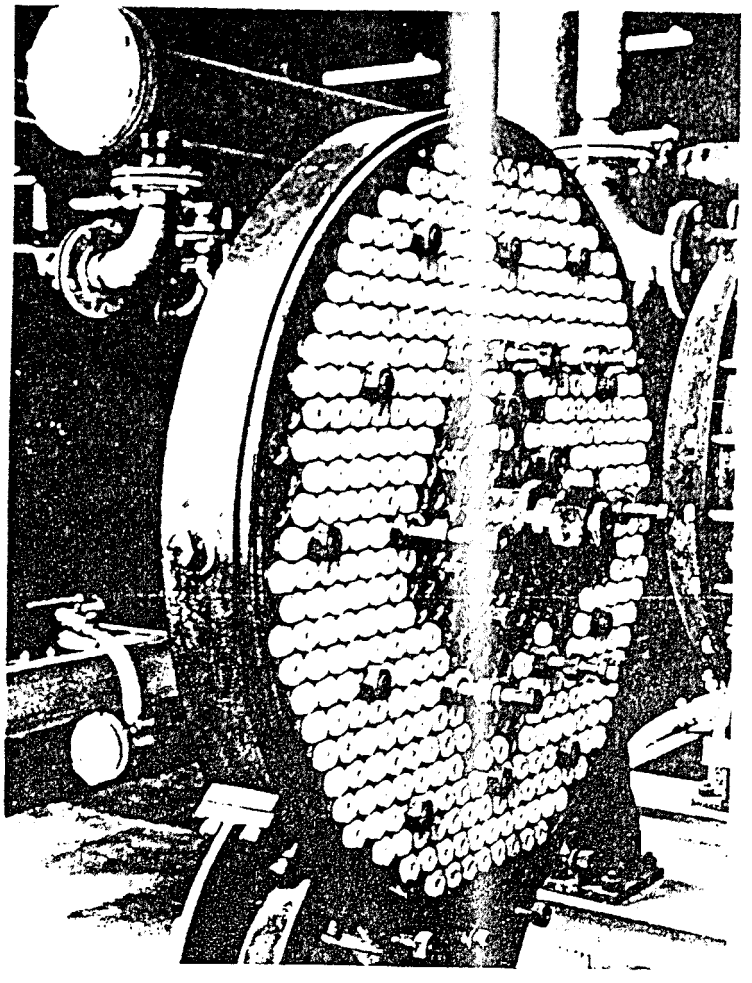


Fig. 30.11. The multiple hydroclones are shown with one housing open, disclosing the stationary, small, relatively short nylon centrifugal devices fed through the side of the housing (not visible in the figure). Individually, the 480 hydroclones are fed tangentially, with the overflow, or lighter gluten, discharged from one housing, and the underflow, or heavier starch, discharged from the other housing. *(Dorr-Oliver.)*

steep-liquor has proved to be a good culture medium for several microorganisms. The by-products, such as gluten from wheat starch manufacture, are used for cattle feed and hydrolyzed to form *hydrolyzed vegetable protein*, a flavoring agent containing the flavor enhancers, glutamic acid and monosodium glutamate. *Gasohol* is being made in converted wet-milling plants in substantial quantity. By 1983, such plants in the United States are slated to produce 1.55×10^9 L of ethanol, a not inconsiderable quantity of motor fuel. Brazil has a very ambitious program to produce alcohol from sugar cane.

MISCELLANEOUS STARCHES

Amylose. Amylose occurs to the extent of 27% in cornstarch, the other 73% being amylopectin. Amylose is a linear chain of dextrose units and resembles cellulose, which it can supplant for many uses, such as in films, adhesives, and paper. Waxy corn is almost all amylose and is being grown in increasing amounts. However, there are a number of processes[28] for separating the two starches (Staley, Corn Products, etc.). One process heats the cornstarch

[28]Staley, Starch Carbohydrates, *Chem. Eng.* 68 (5) 80 (1961).

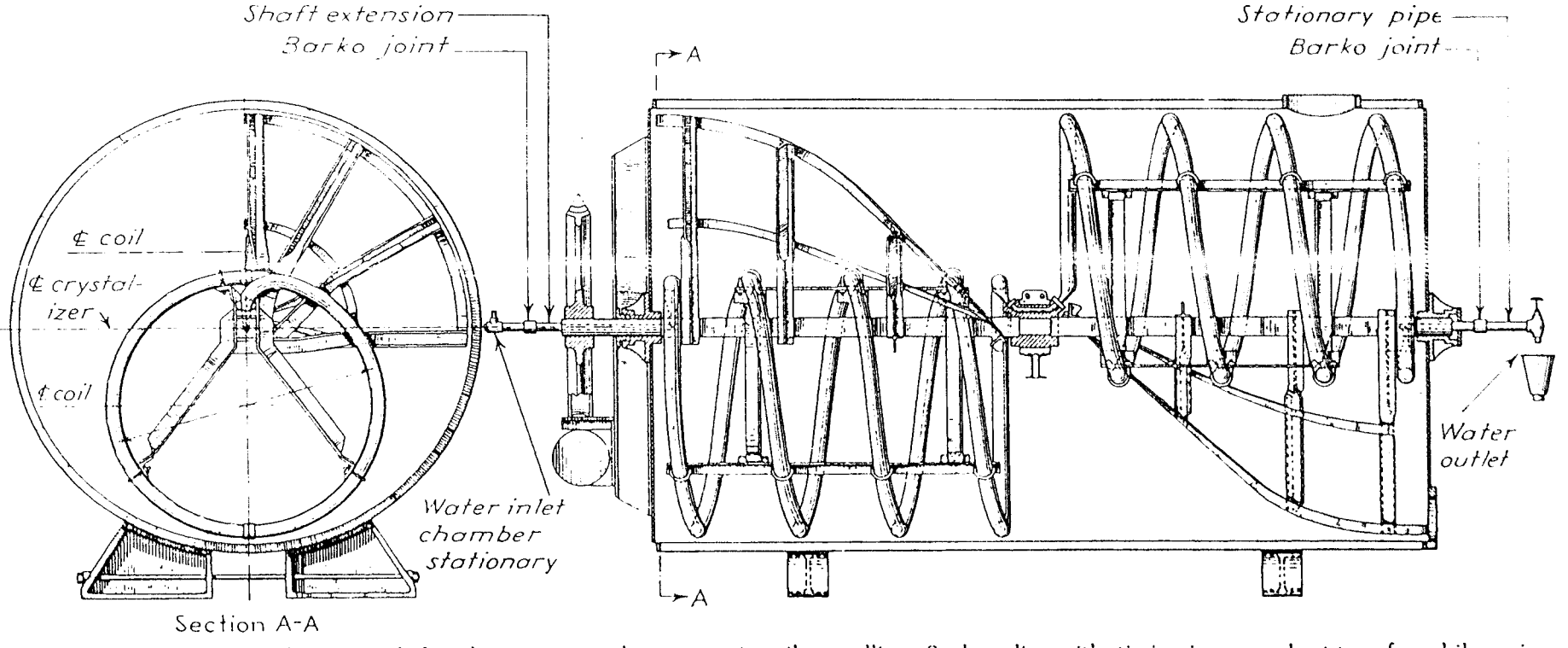


Fig. 30.12. Dextrose crystallizer provided with a scraper and an eccentric coil crystallizer. Such cooling with stirring improves heat transfer while maintaining uniformity in temperature drop. Rotation rate is ⅛ rpm. Crystallization time is about 100 h for dextrose. Water is passed through the coil for cooling. *(Kilby Manufacturing Co.)*

slurry under pressure to prevent boiling, whereupon the mixed starch dissolves; upon slow cooling to about 49°C the amylose crystals form and are recovered, leaving the amylopectin to be precipitated upon further cooling.

White Potato Starch.[29] White potatoes contain 10 to 30% starch. Upon being received at the factory, the potatoes are washed and disintegrated to a water pulp, using a hammer mill. The pulp is treated with sulfur dioxide gas, in the ratio 0.5 kg per kilogram of starch, and sent to a continuous horizontal centrifuge with an imperforate conical bowl and a continuous-spiral-ribbon starch remover. The protein-water mixture is separated from the starch, cellulose, and skins, and the latter three substances are resuspended in water. The suspension is sieved, and the pulp from the sieves is reground and resieved. The liquor from the second sieving is again passed through a centrifuge, suspended in water, and sent to separation devices. From this point on operations are similar to those used for the manufacture of cornstarch (Fig. 30.6). Two other processes are also used. In the batter process, which is similar to Martin's process, the dough formed is dispersed in water and the dispersed gluten collected on a sieve. Using alkali in a similar process disperses the gluten sufficiently that the starch settles out on standing.

Rice Starch. This is made from "cargo rice," which still has the brown outer cuticle attached or from broken white grains rejected as foodstuff. The rice is steeped for 24 h with dilute caustic soda solution (1.005 specific gravity) in tanks with perforated false bottoms. At the end of the period the liquor is withdrawn, the rice washed, fresh liquor added, and steeping continued for another 36 to 48 h. The resulting softened grains are ground with a caustic solution to a specific gravity of 1.24, and the mash is centrifuged. The solids obtained include all sorts of fibrous material, starch, and gluten. These are resuspended, a small amount of formaldehyde is added to inhibit fermentation, and they are recentrifuged and washed. A bleaching or bluing agent may be added at this point. The liquor is screened, adjusted to a specific gravity of 1.21, and sent to disk centrifuges. The resulting starch is dried for 2 days at 50 to 60°C.

Cassava (Tapioca) Starch. This starch is obtained from the roots and tubers of the manioc plant. Imports are mainly from Thailand and Brazil. The average starch content varies from 20 to 30%. In general, the roots are pulped and washed on sieves to obtain the starch. Separating and purifying operations are similar to those described for potato starch.

Sago Starch. This is obtained from the pith of the sago palm, and also from yams in the East Indies and Borneo. Pearl sago starch is made by drying the starch so as to form a plastic dough, which is then forced through sieves and dried in the air.

Other Starch Sources. Sweet potatoes, sorghum, waxy sorghum, and waxy corn are all currently important sources of starch which is obtained from them by methods substantially similar to those described here.

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[29]Knight, op. cit., p. 58.

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Chapter 4

Plastic Industries

The development of plastics from laboratory curiosities to products tailored to industry's needs has brought new and economical materials of construction to the engineer and the designer. Not only can plastics replace metals and other materials, but they can also be used with them. A plastic may be defined as a material that contains a polymerized organic substance of large molecular weight as an essential ingredient, is solid in its finished state, and at some stage in its manufacture or its processing into finished articles can be shaped by flow. The common basic raw materials are coal, petrochemicals, cotton, wood, gas, air, salt, and water. Plastics lend themselves to an exceedingly large number of applications because of their toughness, water resistance, excellent resistance to corrosion, ease of fabrication, and remarkable color range.

The use of a plastic material for a specific application is dependent upon its composition, its particular properties, and the design of the part. Synthetic resins are the largest source of plastics, with cellulose derivatives ranking next. All plastic materials of construction have limitations, but, when properly selected, they can be used with the same degree of assurance as metals and alloys.

HISTORICAL. The development of a commercial phenolic resin in 1909 by Baekland was the start of the synthetic plastic industry. His discovery stimulated the search for other plastics and resulted in an industry that has grown to become one of the nation's top ten in size. The first plastic of industrial significance was cellulose nitrate (Celluloid) and was discovered about the middle of the nineteenth century. It was first used in 1869 by Hyatt who was searching for an ivory substitute.

Cellulose acetate was developed in 1894 as a less flammable material and was used extensively as a base for photographic film and as "dope" for airplane coverings during World War I. From that time on, the introduction of new polymer materials was rapid. Table 34.1 shows the date of discovery and/or commercial introduction of the earlier plastics.

CLASSIFICATION. Plastics are often divided into thermosetting, thermoplastic, oil soluble, and protein products as presented in Tables 34.2 and 34.3. On the basis of derivation, they may be grouped as natural resins, cellulose derivatives, protein products, and synthetic resins. In general, except where noted, synthetic resins formed by condensation polymerization are thermosetting (heat curing produces an infusible or insoluble product), and synthetic resins formed by addition polymerization are thermoplastic (heating softens and cooling hardens). These two polymerization reactions are fundamentally different.

Addition polymerization involves a series of conversions which produce a polymer having a recurring structural unit identical with that of the monomer from which it is formed. Condensation polymerization yields polymers whose recurring units lack certain atoms present in the original monomer. The reaction takes place by the combination of two or more units and the elimination of a small molecule such as water, methanol, or hydrogen chloride. During,

Table 34.1 Early History of Polymers

Polymer	Year Introduced
Cellulose nitrate	1868
Cellulose acetate	1894
Phenol-formaldehyde	1909
Cellulose ethers	1912
Vinyls	1927
Urea-formaldehyde	1929
Acrylates	1931
Furans	1934
Polystyrene	1937
Polyamides	1938
Melamine-formaldehyde	1939
Polyesters	1942
Silicones	1942
Polyethylene	1943
Fluorocarbons	1946
Epoxy	1948
Crystalline polypropylene	1957
Phenoxy	1962

Table 34.2 Types of Resins and Plastics, with Some Common Trade Names

Thermosetting Resins
- Phenolic resins: Bakelite, Durez, Catalin, Formica, Indur
- Amino resins: Plaskon, Beetle, Cymel, Micarta, Melmac
- Alkyd resins: Glyptal, Rezyl, Beckosol, Dulux
- Epoxy resins: Epon, Araldite, Ren, Epocast, Marblette
- Polyester (unsaturated) and allyl resins: Aropol, Atlac, Dapon
- Silicone resins: Pyrotex, Dow Corning
- Polyimides: Vespel, Kapton

Thermoplastic Resins
- Cellulose Derivatives
  - Cellulose nitrate: Celluloid, Pyralin, Nitron
  - Cellulose acetate: Kodapak, Tenite, Plastacele
  - Cellulose propionates: Forticel, Reed
  - Cellulose acetate-butyrates: Tenite II, Kodapak II
  - Ethyl cellulose: Ethocel, Soplasco, Campco
- Polymer Resins
  - Acrylate or polyacrylates: Plexiglas, Lucite, Acryloid
  - Vinyls: Vinylite, Gelva, Butacite, Koroseal, Alvar, PVA
  - Polyvinylidenes: Saran
  - Styrenes: Styron, Lustrex, Loalin
  - Polyamides: Nylon, Zytel, Kevlar, Nomex
  - Polyethers: Penton, Calcon, Delrin
  - Polyethylene: Polyethylene, Poly-Eth, Tygothene, Pentothene
  - Polypropylene: Poly-Pro, Pro-fax
  - Fluorocarbons: Kel-F, Teflon, Fluorosint
  - Polyesters: Mylar, Celanex, Ekonol
  - Polycarbonates: Lexan, Merlon
  - Polysulfones: Udel, Astrel 360, Victrex, Radel

Table 34.3 Classification of Commercial Resins and Plastics by Derivation

I. *Derivatives of Natural Products* (thermoplastic, except where noted)
- A. Natural resins
  - 1. Fossil and plant resins
  - 2. Rosin
  - 3. Shellac
  - 4. Lignin (thermosetting)
- B. Cellulose derivatives
  - 1. Regenerated cellulose
    - *a.* Viscose
    - *b.* Cuprammonium
  - 2. Cellulose esters
    - *a.* Nitrate
    - *b.* Acetate
    - *c.* Propionate
    - *d.* Mixed esters (nitrate-acetate, acetate-propionate, acetate-butyrate)
  - 3. Cellulose esters
    - *a* Methyl
    - *b.* Ethyl
    - *c.* Carboxymethyl
- C. Protein derivatives
  - *a* Casein-formaldehyde
  - *b* Zein (corn protein)-formaldehyde
  - *c* Soybean protein-formaldehyde

II. *Synthetic Resins Formed by Condensation Polymerization* (thermoset, except where noted)
- A. Phenolic resins
  - 1. Phenol-formaldehyde
  - 2. Phenol-furfural
  - 3. Resorcinol-formaldehyde
- B. Amino resins
  - 1. Urea-formaldehyde
  - 2. Melamine-formaldehyde
- C. Polyesters
  - 1. Alkyd
  - 2. Unsaturated or oil-modified alkyds
  - 3. Polycarbonates (thermoplastic)
- D. Polyethers (thermoplastic)
  - 1. Polyformaldehydes
  - 2. Polyglycols
- E. Polyurethanes (thermoplastic under some conditions)
- F. Polyamides (thermoplastic)
- G. Epoxides
- H. Silicone resins (thermoplastic under some conditions)
- I. Ionomers
- J. Polysulfones
- K. Polyimides

III. *Synthetic Resins Formed by Addition Polymerization* (thermoplastic)
- A. Polyethylene
- B. Polypropylene
- C. Polyisobutylene
- D. Fluorocarbon polymers
- E. Polyvinyl acetate and derivatives
  - 1. Polyvinyl alcohol
  - 2. Acetals
- F. Other vinyl polymers
  - 1. Polyvinyl ethers
  - 2. Divinyl polymers
  - 3. Polyvinyl chloride
- G. Polyvinylidene chloride
- H. Polystyrene
- I. Acrylic polymers

or after, the original condensation polymerization, the long chains of polymer may react with each other to form a "cross-linked" material which is usually harder and tougher than the straight-chain polymer. Properties can be varied for special purposes by regulating the amount of cross-linking.

Another variation in the type of final product is effected by the simultaneous polymerization of two or more types of monomers. By carefully regulating the relative amounts of the monomers and reaction conditions and initiators, the properties of the final polymer can be controlled. Three types of copolymers may be formed, depending upon conditions

Random copolymer, $M_1M_2M_2M_1M_1M_1M_2$
Alternating copolymer, $M_1M_2M_1M_2M_1M_2$
Block copolymer, $M_1M_1M_1M_1M_2M_2M_2M_2$

Properties of plastics can be changed by reinforcement with various materials, usually fibers of some sort. Common reinforcing fibers are cellulose fibers, fiberglass, carbon fibers, aramid fibers, and metal filaments. Table 34.4 shows some comparisons between reinforced and unreinforced plastics.

Engineering plastics[1] are high-strength high-performance materials that can be substituted for many metal uses. There are a wide variety of engineering plastics available. Each one has its own special properties, and thus care must be taken in choosing a resin for a particular use. These materials are often the usual plastics but have been carefully manufactured to possess extra quality properties. These materials show better resistance to wear, impact, and corrosive chemicals and have excellent electrical properties. Some of the uses are automobile bumpers and dashboards, pumps, valves, and gears, and driveshafts and transmissions in heavy-duty equipment. Many of the common resins are in use as engineering plastics such as acetal, fluoroplastics, nylon, polyphenylene oxide, polycarbonate, polyphenylene sulfide, polysulfone, polyether-imide, polyethersulfone and nylon-polyether block amides, and several other copolymers.

The common names of plastics are usually the common or even the principal trade names and often are referred to by abbreviations. Some of the international abbreviations are given in Table 34.5.

USES AND ECONOMICS. Plastics are not interchangeable. Each one has its own individual properties and characteristics that make it useful for certain applications. Table 34.6 lists properties and applications for the major commercially produced materials. Tables 34.7 and 34.8 list the selling prices and U.S. production of various representative materials.

RAW MATERIALS

Chemical Intermediates[2] and Monomers

PHENOL.[3] Phenol has been made, over the years, by a variety of processes. Many of the companies producing it use it internally and do not sell it on the open market. The principal

[1]Engineering Plastics, *Chem. Eng.* 89 (16) 42 (1982); *Mod. Plast.* 59 (1) 62 (1982); *Plast. Eng.* 38 (1) 17 (1982).

[2]As in other chapters, intermediates are presented whose chief consumption is in a chemical process industry covered by another chapter.

[3]ECT, 3d ed., vol. 17, 1981, p. 373.

Table 34.4 Comparison of Some Unreinforced and Reinforced Plastics

	Nylon 6/6			Polyester			Polysulfone		
	Unreinforced	40% C Fiber	40% Glass Fiber	Unreinforced	30% C Fiber	30% Glass Fibers	Unreinforced	30% C Fibers	30% Glass Fibers
Specific gravity	1.14	1.34	1.46	1.32	1.47	1.52	1.24	1.37	1.45
Water absorption, 24 h %	1.6	0.4	0.6	0.08	0.06	0.04	0.20	0.15	0.20
Tensile strength, MPa	81	276	214	55	138	134	70	131	124
Flexural strength, MPa	103	414	290	896	200	193	106	176	165
Tensile elongation, %	10	3–4	2–3	10	2–3	3–4	50–100	2–3	3–4
Shear strength, MPa	66	96	83	55		55	62	48	65
Heat distortion temp at 1820 kPa, °C	65	260	260	68	221	221	173	184	184

SOURCE Katz and Milewski (eds.), *Handbook of Fillers and Reinforcements for Plastics*, Van Nostrand Reinhold, New York, 1978

Table 34.5 International Abbreviations for Names of Plastics

Abbreviation	Name of Plastic
CA	Cellulose acetate
CPVC	Chlorinated poly(vinyl chloride)
MF	Melamine-formaldehyde resins
NBR	Poly(acrylonitrile-co-butadiene)
PAN	Polyacrylonitrile
PC	Bisphenol A polycarbonate
PE	Polyethylene
PETP	Poly(ethylene terephthalate)
PF	Phenol-formaldehyde resins
PIB	Polyisobutylene
PMMA	Poly(methyl methacrylate)
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PUR	Polyurethane
PVAC	Poly(vinyl acetate)
PVAL	Poly(vinyl alcohol)
PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)
PVDC	Poly(vinylidene chloride)
PVDF	Poly(vinylidene fluoride)
PVP	Poly(vinyl pyrrolidone)
UF	Urea-formaldehyde resins

SOURCE: Fried, Polymer Technology, Part 1, *Plast. Eng.* 38 (6) 54 (1982).

process in use in the United States is the peroxidation of cumene (isopropyl benzene).

$$\underset{\text{Cumene}}{C_6H_5CH(CH_3)_2} \xrightarrow[130°C]{\text{air + cat}} \underset{\text{Cumene hydroperoxide}}{C_6H_5C(CH_3)_2OOH} \xrightarrow[55\text{–}65°C]{10\text{–}25\%\ H_2SO_4} \underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Acetone}}{CH_3COCH_3}$$

The conversion of cumene to cumene hydroperoxide gives a 25 to 50 percent yield per pass (Fig. 34.1). The cumene hydroperoxide, which has the dangerous explosive properties of other hydroperoxides, decomposes into acetone and phenol in the presence of sulfuric acid. The by-product acetone dominates the acetone market. Phenol can be prepared from toluene, and one small plant in the United States produces it this way. This process is more widely used in Europe.

$$\underset{\text{Toluene}}{C_6H_5CH_3} + 1.5\ O_2 \xrightarrow[\text{Co salt}]{150°C} \underset{\text{Benzoic acid}}{C_6H_5COOH} + H_2O$$

$$C_6H_5COOH + 0.5O_2 \xrightarrow[230°C]{\text{CuMg salts}} \underset{\text{Phenol}}{C_6H_5OH} + CO_2$$

Table 34.6 Summary of Resin Properties and Applications

Resin Type	Properties	Applications
Phenolics	Good strength, heat stability, and impact resistance, high resistance to chemical corrosion and moisture penetration, machinability	Impregnating resins, brake lining, rubber resins, electrical components, structural board, laminates, glues, adhesive binders, molds
Aminos	Good heat resistance, solvent and chemical resistance, extreme surface hardness, resistance to discoloration	Molding compounds, adhesives, laminating resins, paper coating, textile treatments, plywood, dinnerware, decorating structures
Polyesters	Extreme versatility in processing, excellent heat, chemical, and flame resistance, low cost; excellent mechanical and electrical properties	Construction, auto-repair putty, laminates, skis, fishing rods, boats and aircraft components, coatings, decorative fixtures, bottles
Alkyds	Excellent electrical and thermal properties, versatility in flexibility or rigidity, good chemical resistance	Electrical insulation, electronic components, putty, glass-reinforced parts, paints
Polycarbonates	High refractive index, excellent chemical, electrical, and thermal properties; dimensional stability; transparent; self-extinguishing; resistant to staining; good creep resistance	Replacement for metals, safety helmets, lenses, electrical components, photographic film, die casting, insulators
Polyamides	Tough, strong, and easily moldable; light; abrasion-resistant; low coefficient of friction; good chemical resistance; self-extinguishing	Unlubricated bearings, fibers, gears, appliances, sutures, fishing lines, tires, watch straps, packaging, bottles
Aromatic polyamides	High-temperature resistance	Reinforcement of organic matrices
Polyimides	High-temperature resistance	Molded parts, films, and laminating resins for high temperature use up to 180°C
Polyurethanes	Extreme versatility when combined with other resins, good physical, chemical, and electrical properties	Insulation, foam inner liners for clothing, rocket fuel binders, elastomers, adhesives
Polyethers	Excellent corrosion resistance to common acids, alkalies, and salts; can be seam-welded and machined to fit any type, shape, or size of structure	Coatings, pump gears, water-meter parts, bearing surfaces, valves
Epoxies	Excellent chemical resistance, good adhesion properties, strong and tough with low shrinkage during cure, excellent electrical properties, good heat resistance	Laminates, adhesives, flooring, linings, propellers, surface coatings, filament-wound structures (rocket cases)
Silicones	Good thermal and oxidative stability, flexible, excellent electrical properties, general inertness	Mold-release agents, rubbers, laminates, encapsulating resins, antifoaming agents, water-resistant uses
Ionomers	Excellent toughness, abrasion resistance, and transparency, outstanding low-temperature flexural properties	Skin and blister packaging, heel lifts, shoes, ski boots, automobile bumpers, golf ball covers
Phenoxies	Ease in molding, good heat stability, low mold shrinkage, self-extinguishing, good cold flow	Surface coatings, adhesives, binders, electronic parts
Polyethylene	Excellent chemical resistance, low power factor, poor mechanical strength, outstanding moisture-vapor resistance, wide degree of flexibility	Packaging films and sheets, containers, wire cable insulation, pipe, linings, coatings, molds, toys, housewares

(cont. next page)

Table 34.6 Summary of Resin Properties and Applications (*continued*)

Resin Type	Properties	Applications
Polypropylene	Colorless and odorless, low density; good heat resistance, "unbreakable," excellent surface hardness, excellent chemical resistance, good electrical properties	Housewares, medical equipment (can be sterilized), appliances, toys, electronic components, tubing and pipe, fibers and filaments, coatings
Polybutylene	Excellent resistance to abrasive slurries, good chemical resistance, tough, better heat resistance than polyethylene	Pipe and tubing, films, and in blends to lend strength and toughness
Fluorocarbons	Low coefficient of friction, low permeability, low moisture absorption, exceptional chemical inertness, low dielectric strength	Electrical insulation, mechanical seals, gaskets, linings for chemical equipment, bearings, frying-pan coatings, cryogenic applications
Polyvinyl chloride	Excellent physical properties, excellent chemical resistance, ease of processing, relatively low cost, self-extinguishing, ability to be compounded with other resins	Pipe and tubing, pipe fittings, adhesives, raincoats and baby pants, building panels, wastepaper baskets, weather stripping, shoes
Acrylics	Crystal clarity, outstanding weatherability, fair chemical resistance, good impact and tensile strength, resistant to ultraviolet exposure	Decorative and structural panels, massive glazing domes, automotive lens systems, illuminated translucent floor tiles, windows, and canopies, signs, coating, adhesives, elastomers
Polystyrene	Low cost, ease of processing, excellent resistance to acids, alkalies, salts; softened by hydrocarbons; excellent clarity, versatility	Insulation, pipe, foams, cooling towers, thin-walled containers, appliances, rubbers, automotive instruments and panels
Cellulosics	Outstanding toughness, high impact strength, high dielectric strength, low thermal conductivity, high surface luster	Textile and paper finishes, thickening agents, magnetic tapes, packaging, pipe
Furanes	Excellent resistance to both acids and bases, good adhesive properties	Laminates, coatings, impregnants, linings for rocket fuel tanks, floor tiles, abrasive wheels

SOURCES: *Modern Plastics Encyclopedia*, 1981–1982; *Chem. Eng. Prog.* 76 (1) 57 (1980).

Table 34.7 Selling Price of Various Resins

	Average Selling Price, dollars per kilogram					
Type	1937	1954	1964	1971	1981	1982
Polyethylene	—	0.97	0.46	0.26	1.03	0.88
Vinyls	1.52	0.90	0.64	0.35	0.70	0.70
Styrenes	1.58	0.68	0.46	0.42	1.12	0.99
Phenolics	—	0.57	0.53	0.46	0.99	0.99
Polyesters	—	—	0.68	0.51	1.34	1.17
Urea and melamines	1.21	0.53	0.57	0.77	1.28	1.03
Alkyds	0.44	0.66	0.57	0.77	1.28	1.03
Polyamide (nylon)	—	3.52	2.05	1.21	3.19	—
Polypropylene	—	—	0.53	0.29	0.88	1.17
Epoxy resins	—	—	1.30	1.01	2.20	2.77

SOURCE: *Synthetic Organic Chemicals*, U.S. Tariff Commission.

Table 34.8 Plastics and Resins, U.S. Production (in metric tons)

Material	1974	1979	1981
Polyethylene			
High density	128,700	221,950	212,420
Low density	270,936	354,488	340,925
Polypropylene		176,632	176,496
Polyvinyl alcohol	64,400	61,235	61,236
Polyvinyl chloride	220,000	278,420	255,467
Styrene resins	188,335	181,300	163,430
Phenolics	60,555	78,605	58,510
Polyesters	41,320	58,350	44,270
Urea and melamines	45,360	70,170	59,740
Epoxies	11,290	17,795	17,795

SOURCES: *Chem. Eng. News* 60 (8) 6 (1982); 60 (35) 10 (1982); *Chem. Mark. Rep.* October 19, 1981

In 1982 almost 1×10^9 kg was produced in the United States at a price of 70 to 75 cents per kilogram.[4]

FORMALDEHYDE.[5] Formaldehyde results from the exothermic oxidation and endothermic dehydrogenation of methanol as shown in Fig. 34.2.

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow{Ag} CH_2O + H_2O \qquad \Delta H = -156 \text{ kJ}$$
$$CH_3OH \rightarrow CH_2O + H_2 \qquad \Delta H = +85 \text{ kJ}$$

These two reactions occur simultaneously in commercial units in a balanced reaction, called autothermal because the oxidative reaction furnishes the heat to cause the dehydrogenation to take place. About 50 to 60 percent of the formaldehyde is formed by the exothermic reaction. The oxidation requires 1.6 m^3 of air per kilogram of methanol reacted, a ratio that is

[4]Key Chemicals, *Chem. Eng. News* 60 (31) 10 (1982).

[5]Walker, *Formaldehyde*, ACS Monograph 159, Reinhold, New York, 1964; Austin, Industrially Significant Organic Chemicals, *Chem. Eng.* 81 (11) 101 (1974); Diem, Formaldehyde Routes Bring Cost, Production Benefits, *Chem. Eng.* 85 (5) 83 (1978); ECT, 3d ed., vol. 11, 1981, p. 231.

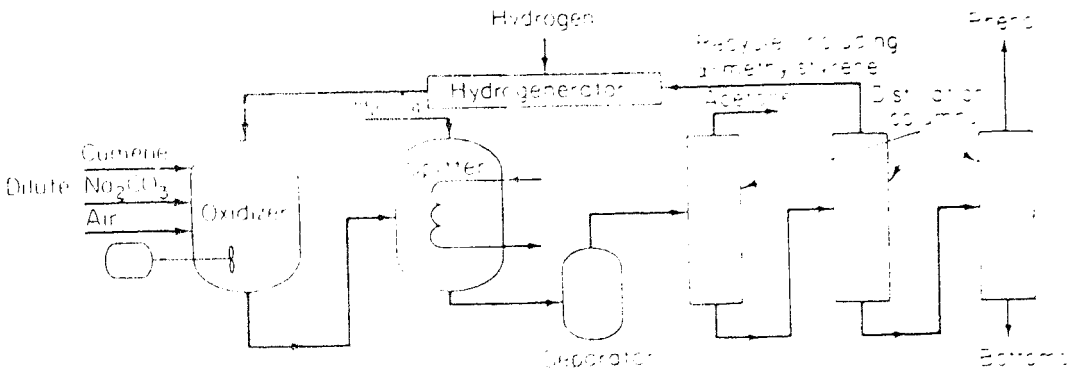


Fig. 34.1. Phenol from cumene production flowchart

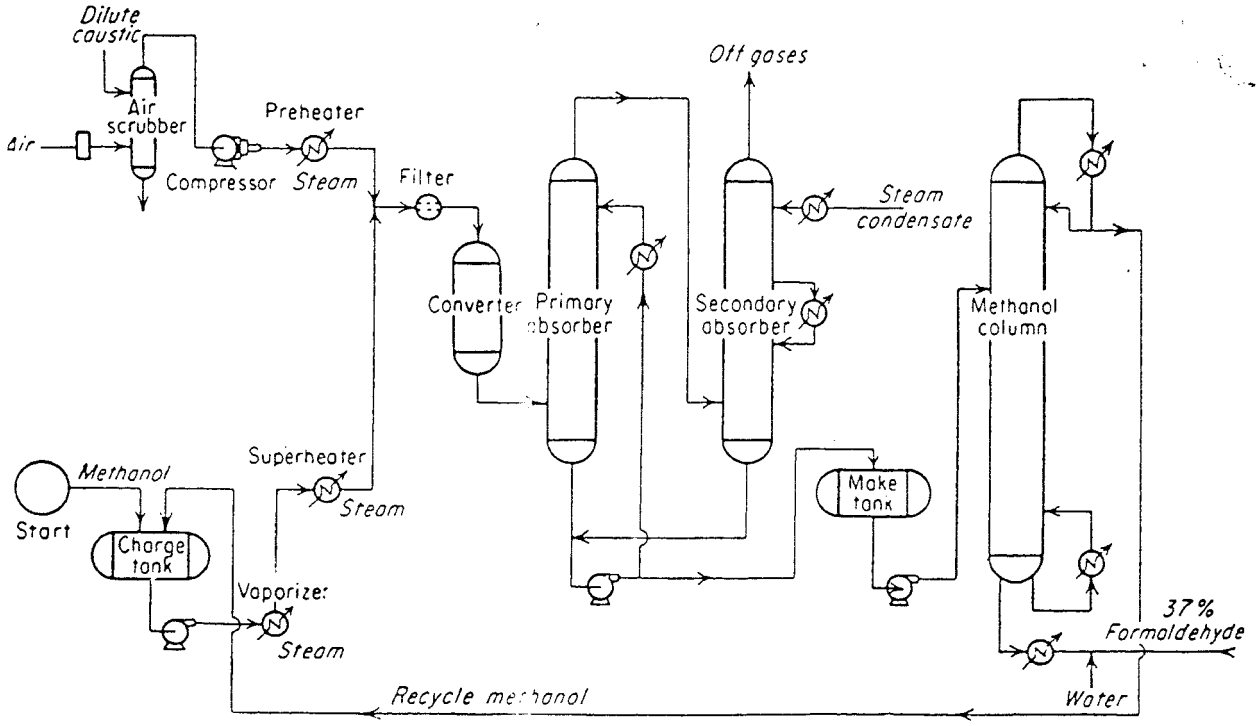
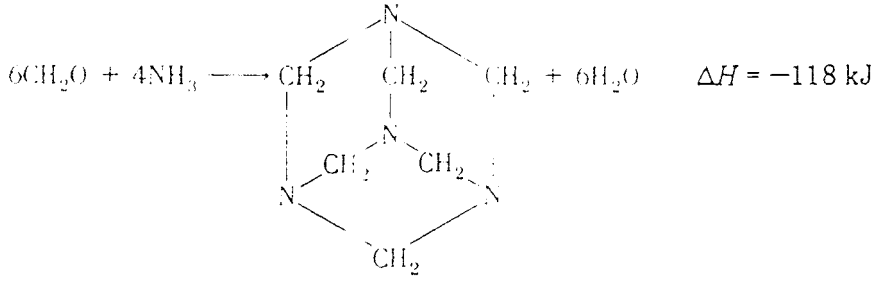


Fig. 34.2. Flowchart for the manufacture of formaldehyde.

maintained when passing separate streams of these two materials forward. Fresh and recycle methanol are vaporized, superheated, and passed into the methanol-air mixer. Atmospheric air is purified, compressed, and preheated to 54°C in a finned heat exchanger. The products leave the converter at 620°C and at 34 to 69 kPa absolute. The converter is a small water-jacketed vessel containing the silver catalyst. About 65 percent of the methanol is converted per pass. The reactor effluent contains about 25% formaldehyde, which is absorbed with the excess methanol and piped to the make tank. The latter feeds the methanol column for separation of recycle methanol overhead, the bottom stream containing the formaldehyde and a few percent methanol. The water intake adjusts the formaldehyde to 37% strength (marketed as formalin). The yield from the reaction is 85 to 90 percent. The catalyst is easily poisoned so stainless-steel equipment must be used to protect the catalyst from metal contamination.

In 1982 about 2.2×10^6 t of 37% solution (formalin) was produced in the United States at a price of 19 to 20 cents per kilogram.[6,6a]

HEXAMETHYLENETETRAMINE. Evaporation of the reaction product of formaldehyde and ammonia produces hexamethylenetetramine.



[6]Key Chemicals, *Chem. Eng. News* 60 (13) 26 (1982).

[6a]t = 1000 kg.

This compound finds use as a urinary antiseptic (Urotropine), in the rubber industry, in the preparation of the explosive cyclonite (Chap. 22), and mainly in making phenol-formaldehyde resins, where it is known as "hexa."

VINYL ESTERS. The addition of acids to acetylene furnishes esters.

$$CH{\equiv}CH + CH_3COOH \rightarrow \underset{\text{Vinyl acetate}}{CH_3COOCH{=}CH_2} \qquad CH{\equiv}CH + HCl \rightarrow \underset{\text{Vinyl chloride}}{CH_2{=}CHCl}$$

If two molecules of acid react, a compound such as 1,1-ethane diacetate is formed:

$$CH{\equiv}CH + 2CH_3COOH \rightarrow (CH_3COO)_2CHCH_3$$

Vinyl chloride is usually prepared by the oxychlorination (dehydrochlorination) of ethylene.[7] See Fig. 34.3 which presents a flowchart for the following reactions.

CHLORINATION

$$CH_2{=}CH_2 + Cl_2 \rightarrow \underset{\text{Dichloroethane}}{CH_2ClCH_2Cl}$$

OXYCHLORINATION

$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 + 2HCl \xrightarrow{CuCl_2} CH_2ClCH_2Cl + H_2O$$

DEHYDROCHLORINATION

$$\underset{\text{Dichloroethane}}{CH_2ClCH_2Cl} \xrightarrow{\text{cracking furnace}} \underset{\text{Vinyl chloride}}{CH_2{=}CHCl} + HCl$$

[7]Austin, The Industrially Significant Organic Chemicals, *Chem. Eng.* 81 (6) 87 (1974); *Encyclopedia of Polymer Science and Technology*, Wiley, New York, 1964–1971 (referred to hereafter as EPST), vol. 16, 1971, p. 315; *Hydrocarbon Process.* 60 (11) 235 (1981).

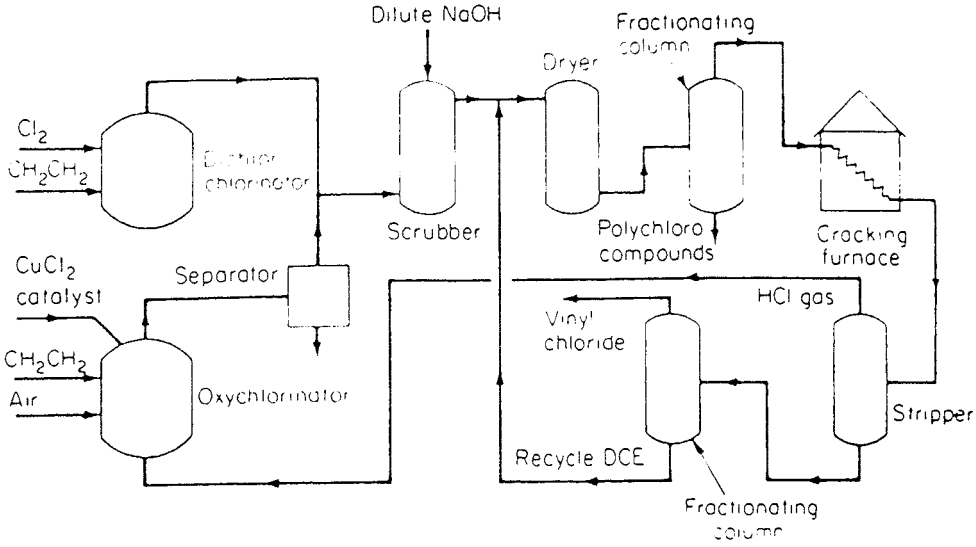


Fig. 34.3. Flowchart for the production of vinyl chloride

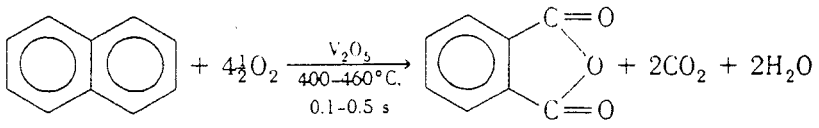
The $CuCl_2$ catalyst (on an inert fixed carrier) may react as follows:

$$CH_2{=}CH_2 + 2CuCl_2 \rightarrow CH_2ClCH_2Cl + Cu_2Cl_2$$
$$Cu_2Cl_2 + \tfrac{1}{2}O_2 \rightarrow CuO \cdot CuCl_2$$
$$CuO \cdot CuCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

Exposure to vinyl chloride vapors, even in very small concentrations, causes some workers to develop liver cancer. The government requires that worker exposure to vinyl chloride monomer be no more than 1 ppm over an 8-h period, and no more than 5 ppm for any 15-min period. To achieve this requires extensive and expensive pollution-abatement systems.[8]

Vinyl acetate[9] is also made from ethylene in a vapor phase process. The feed mixture is ethylene, acetic acid, and oxygen, and is circulated through a fixed-bed tubular reactor. The catalyst is a noble metal, probably palladium, and has a life of several years.

PHTHALIC ANHYDRIDE.[10] Phthalic anhydride is one of the most important intermediates for the plastics industry. Figure 34.4 lists the end-use pattern of this compound. The processes for the preparation of phthalic anhydride are controlled oxidation of *o*-xylene or naphthalene.



Oxidation is one of the very useful chemical conversions in organic technology. The cheapest agent is air, but oxygen is sometimes employed. For liquid-phase reactions a great many oxidizing agents are in industrial use, such as nitric acid, permanganates, pyrolusite, dichromates, chromic anhydride, hypochlorites, chlorates, lead peroxide, and hydrogen peroxide. Water and carbon dioxide and many other oxidized substances are the by-products of the main oxidation. When charcoal or carbon (amorphous) changes to carbon dioxide $\Delta H = -404$ kJ/g-mol,[11] and when hydrogen burns to water (gaseous), $\Delta H = -242$ kJ/g-mol. These energy changes, although the basis of combustion, frequently accompany controlled oxidation, as in the making of phthalic anhydride and maleic acid. In most oxidations, even when the formation of carbon dioxide and water can be repressed, the energy change is exothermic and large. This requires particular care in the design and construction of the equipment to ensure efficient heat transfer and to prevent the controlled oxidation from becoming combustion.

The naphthalene process, with a suitable catalyst, was discovered by Gibbs and Conover.[12]

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[8]Bertram, Minimizing Emissions from Vinyl Chloride Plants, *Environ. Sci. Techol.* 11 864 (1977).

[9]Carron and Galloway, Vinyl Acetate from Ethylene, *Chem. Eng.* 80 (9) 92 (1973); *Hydrocarbon Process.* 60 (11) 233 (1981); *Modern Plastics Encylopedia*, 1981–1982 (referred to hereafter as MPE).

[10]ECT, 3d ed., vol. 17, 1982, pp. 738–746.

[11]For carbon, the equivalent kJ/kg = −32,560; for hydrogen, −120,950.

[12]U.S. Patent 1,285,217 (1918).

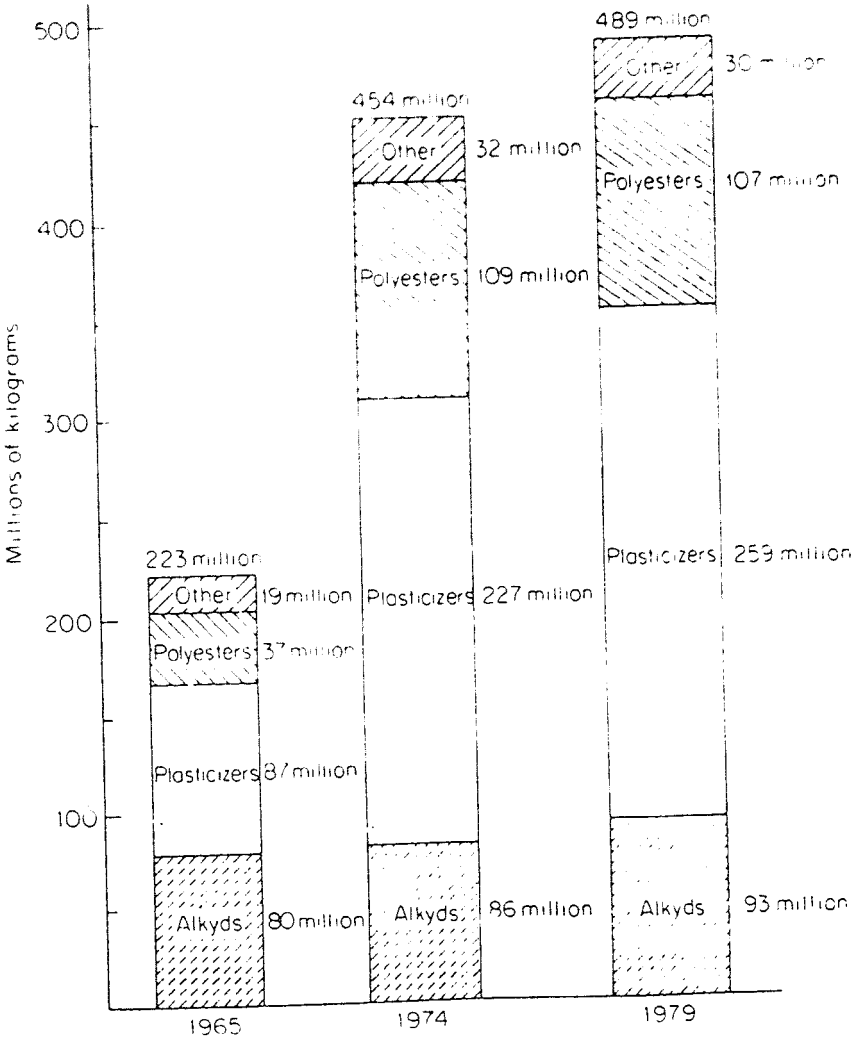

Fig. 34.4. Phthalic anhydride end-use pattern

It was also necessary to work out efficient equipment to remove the great amount of heat liberated and to keep the temperature within favorable narrow limits. One of the successful devices was that patented by Downs[13] and depicted in principle in Fig. 34.5. In the Downs reactor the temperature is controlled by raising or lowering the boiling point of mercury by raising and lowering the pressure of an inert gas (nitrogen) on the mercury boiling and condensing system. Other heat-transfer media have been proposed, such as water, sulfur, diphenyl, diphenyl oxide, mercury amalgams, and mixed molten nitrate-nitrite. The products from the reaction are rapidly cooled to about 125°C (approximately the dew point of phthalic anhydride) and then sublimed or distilled.

Fundamental changes have been made in the manufacture of phthalic anhydride. The first was a change in the source of the naphthalene. The dwindling supply from coal tar was supplemented by developing a purer one from petrochemicals by demethylating methylnaphthalenes (Chap. 37). The second change was to use a fluidized bed of the catalyst V_2O_5 instead of the long successful fixed bed. The third change was the use of *o*-xylene in either of the above procedures. A fourth change was to develop other catalysts which would work

[13]U.S. Patent 1,604,739 (1926); 1,789,909 (1931); 1,873,676 (1932).

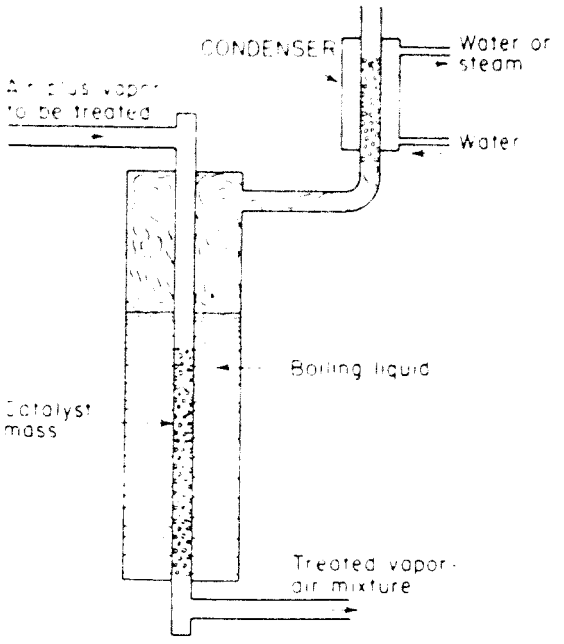

Fig. 34.5. Apparatus for the removal of reaction heat by the boiling of a liquid

favorably on either naphthalene or *o*-xylene. The fifth change involved removing the large heat of reaction by using a molten salt bath. This made it possible to recover some of this heat of reaction to generate steam. Certain of these changes are illustrated in Fig. 34.6 for a fixed-bed process, and more details are available in the references.[14]

If naphthalene is burned completely to carbon dioxide and water, 41,870 kJ/kg of naphthalene is liberated. For naphthalene conversion to phthalic anhydride, $\Delta H = -12{,}700$ kJ/kg of naphthalene oxidized. During the actual operation of this reaction an exothermic reaction of from 14,000 to more than 23,000 kJ/kg of naphthalene occurs, owing to an amount of complete combustion that always takes place.

Modern modifications of the process have been made to reduce the amount of energy required. These low-energy processes increase the hydrocarbon-to-air loadings so that they

[14] Zimmer, Low Air-Feedrate Cuts Phthalic Anhydride Costs, *Chem. Eng.* 81 (5) 82 (1974); Phthalic Anhydride Made with Less Energy, *Chem. Eng.* 86 (3) 62 (1979); Dow and Miserlis Recover Power from Phthalic Plants, *Hydrocarbon Process.* 56 (4) 167 (1977).

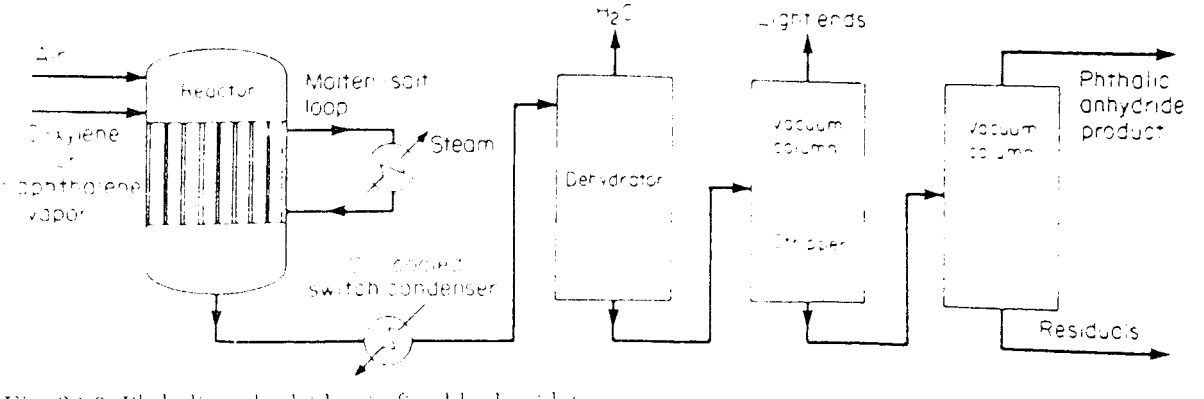

Fig. 34.6. Phthalic anhydride via fixed bed oxidation.

are in the explosive range. The lower explosive limit for *o*-xylene- or naphthalene-air mixtures is 43 g/m^3 at STP, but the processes operate at 60 g/m^3 air at STP. The reactor has been designed to withstand explosions and the catalyst, V_2O_5 plus TiO_2 on an inert carrier, serves to deter an explosion. It is claimed that electrical requirements have been cut from 3300 to 600 MJ per metric ton of anhydride produced and the fuel-oil requirements have been eliminated.

METHYL ACRYLATE AND METHACRYLATE.[15] Methyl and ethyl acrylate and methyl, ethyl, and butyl methacrylate monomers are manufactured in large tonnages. The procedures for preparing acrylate resins, following the Dow-Badische-Reppe synthesis, are based on the reaction:

$$CH_2{=}CH_2 + CO + ROH \rightarrow CH_2CH{-}COOR$$

The conventional method of preparing methyl methacrylate, MMA, has been by the reaction of hydrogen cyanide with acetone and subsequent treatment with methyl alcohol.

$$CH_3COCH_3 + HCN \longrightarrow CH_3\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}{-}CN \xrightarrow[H_2SO_4]{CH_3OH} CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}COCH_3$$

The newest process for producing MMA uses a catalytic oxidation of isobutylene or *tert*-butyl alcohol, claimed to give yields of 70 percent. At present, however, *tert*-butyl alcohol is more valuable as an octane enhancer in gasoline, so the cyanohydrin process will continue to be used.

Other Raw Materials

NATURAL PRODUCTS. *Cellulose*, the structural material of the plant world, is itself a polymer composed of 50 to 100 units of the disaccharide cellobiose. Cellobiose on hydrolysis yields two molecules of glucose and is similar to maltose. However, maltose is an α-glucoside while cellobiose is a β-glucoside. The separation and purification of cellulose is discussed in Chap. 33.

PLASTICIZERS. Plasticizers are organic compounds added to plastics to improve workability during fabrication, to extend or modify the natural properties of the plastics, and to develop new, improved properties not present in the original resin. Plasticizers reduce the viscosity and make shaping and forming easier. They also impart flexibility and other desired properties to the finished product.

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[15]ECT, 3d ed., vol. 1, 1978, pp. 386–409; *MPE*, 1981–1982; *Chem. Eng. News* **59** (30) 37 (1981); *Chem. Week* **129** (5) 37 (1981).

FILLERS AND REINFORCEMENTS. Many materials may be added to plastics to increase strength, thermal conductivity, resistance to heat distortion, and lower thermal expansion. Table 34.9 classifies the various fillers and reinforcements that are in use. Formerly asbestos was used, but due to its human carcinogenic properties, it is no longer an acceptable filler.

MANUFACTURING PROCESSES[16]

General Polymerization Processes

BULK POLYMERIZATION. Polymerization of the monomer in bulk may be carried out in the liquid or vapor state. The monomers and activator are mixed in a reactor and heated or cooled as needed. As most polymerization reactions are exothermic, provision must be made to remove the excess heat. In some cases, the polymers are soluble in their liquid monomers, causing the viscosity of the solution to increase greatly. In other cases, the polymer is not soluble in the monomer and it precipitates out after a small amount of polymerization occurs.

[16]Driver, *Plastics Chemistry and Technology*, Van Nostrand Reinhold, New York, 1979.

Table 34.9 Classification of Fillers and Reinforcements

Organic Origin	Inorganic Origin
Cellulosic	Mineral fillers
Wood flour	Calcium carbonate
Shell flour	Mica
Cotton	Kaolin
α-Cellulose	Silica
Paper pulp	Talc
Shredded textiles	Carbide
Sisal	Metallic oxides
Carbonaceous	Sulfates
Graphite filaments	Silicates
Carbon blacks	Titanates
Synthetic	Powdered metals
Aramid yarns and fibers	Iron
	Lead and zinc
	Copper
	Aluminum
	Filaments
	Fiberglass
	Basalt fibers
	Boron and other metals
	Aluminum oxide

SOURCE: Katz and Milewski (eds.), *Handbook of Fillers and Reinforcements for Plastics*, Van Nostrand Reinhold, New York, 1978.

SOLUTION POLYMERIZATION. This method is often used when the exothermic heat is too great to be controlled in bulk polymerization. The monomer and initiator are dissolved in a nonreactive solvent which serves to slow the reaction and thus moderate the heat given off. The heat evolved may be controlled by refluxing the solvent. The polymer concentration usually has to be low to avoid too high a viscosity. This method produces polymers of low to medium molecular weight.

SUSPENSION POLYMERIZATION. In this process the monomer is suspended in water by agitation, and stabilizers such as talc, fuller's earth, and bentonite are added to stabilize the suspension and prevent polymer globules from adhering to each other. Normally, the initiator is soluble in the monomer. Each monomer globule polymerizes as a spherical pearl of high molecular weight. The heat of polymerization is removed by the water, permitting accurate temperature control. The stabilizer must be separated from the polymer, and sometimes, because of partial miscibility of the monomer and water, subsidiary polymerization may occur in the aqueous phase, producing a low molecular weight polymer.

EMULSION POLYMERIZATION. This is similar to suspension polymerization but the monomer is broken up into droplets that form aggregates called micelles. The monomer is on the interior of the micelles, and the initiator is in the water. Soap, or another emulsifying agent, is used to stabilize the micelles. The initiator diffuses into the micelle to start polymer growth. Emulsion polymerizations are rapid and can be carried out at relatively low temperatures. The aqueous phase absorbs the heat evolved by the reaction. Polymers of very high molecular weight can be prepared by this process.

Condensation-Polymerization Products

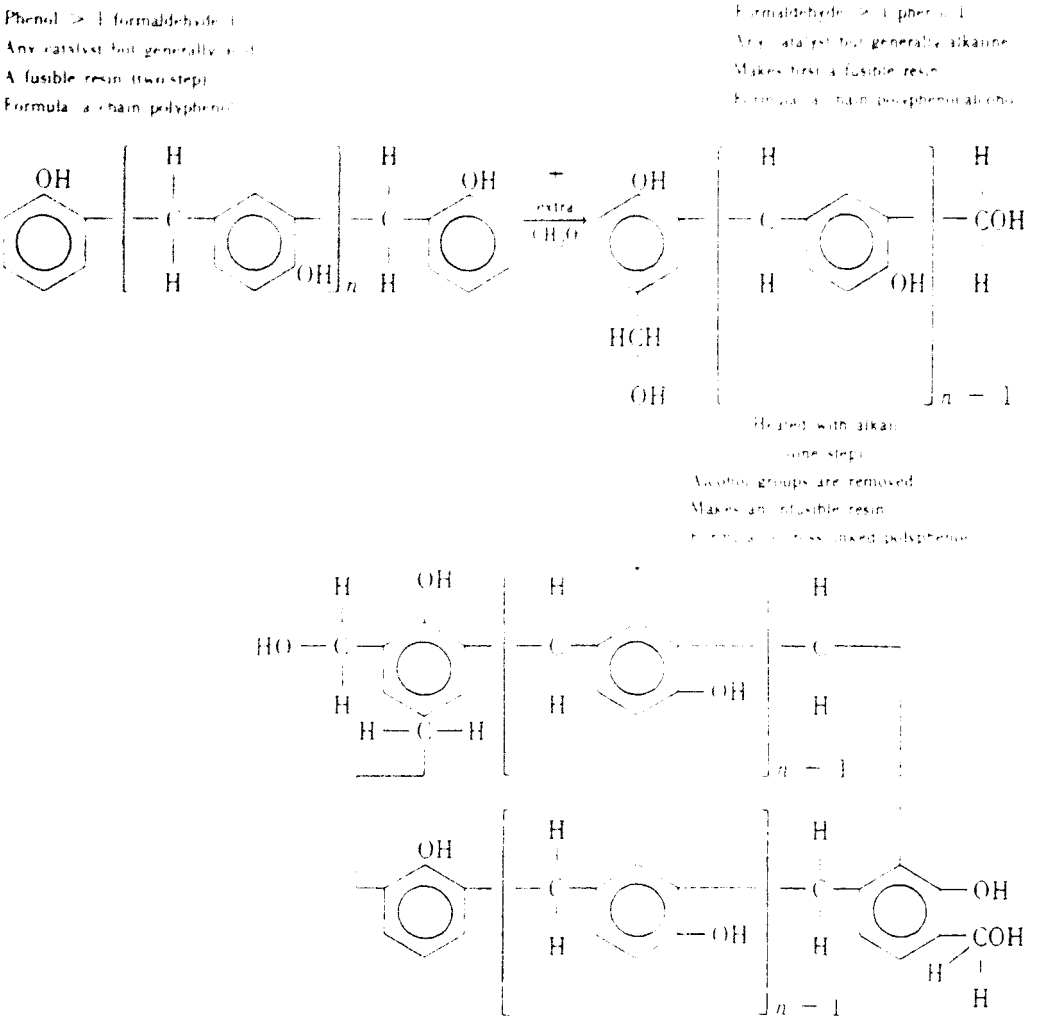
PHENOLICS. Phenolic resins designate a group of synthetic resins that are probably the most varied and versatile that we know. They may be made from almost any phenolic body and an aldehyde. Phenol-formaldehyde resins constitute by far the greatest proportion, but phenol-furfural, resorcinol-formaldehyde, and similar resins are also included in this group. The product obtained depends primarily on the concentration and chemical nature of the reactants, the nature and concentration of the catalyst used, the temperature and reaction time, and the modifying agents, fillers, and extenders. The initial reaction between the phenol and a mixture of cresols with formaldehyde, using an alkaline catalyst, produces benzyl alcohols:

$$C_6H_5OH + CH_2O \rightarrow o\text{- or } p\text{-}C_6H_4OH \cdot CH_2OH$$

Simultaneously, additional formaldehyde may react to produce both di- and trimethylolphenols. These alcohols continue to condense and polymerize with each other rapidly and almost violently.[17]

[17]Butler, Phenol Resin Emulsions, *Am. Dyest. Rep.*, 32 128 (1943); *EPST*, Wiley, New York, 1964.

Phenol-formaldehyde Reactions: Condensations and Polymerizations

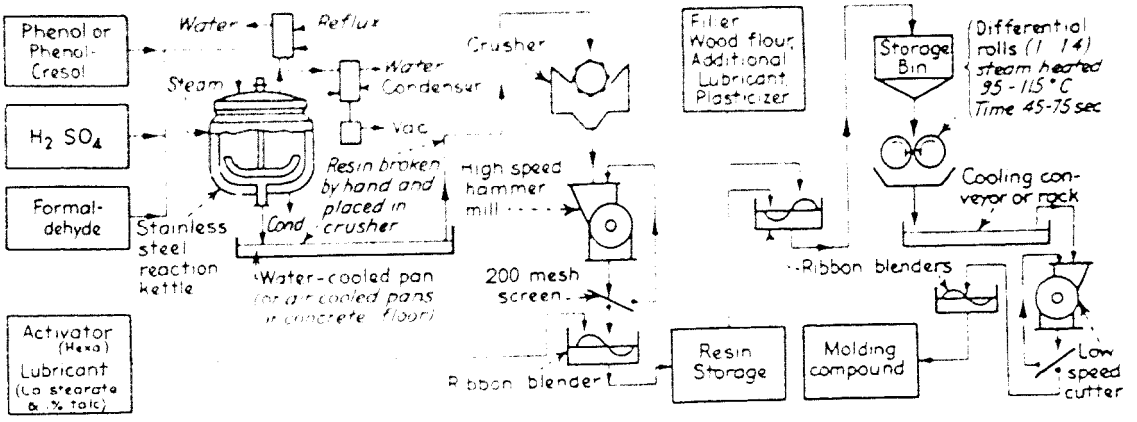


These resins, when classified according to the nature of the reaction occurring during their production, are one of two fundamental types.

1. *One-step resins.* In these, all the necessary reactants (phenol, formaldehyde, catalyst required to produce a thermosetting resin are charged into the resin kettle in the proper proportions and react together. An alkaline catalyst is used. The resin, as discharged from the kettle, is thermosetting or heat-reactive and requires only further heating to complete the reaction to an infusible, insoluble state.

2. *Two-step resins.* Only part of the necessary formaldehyde is added in the kettle in making these resins, and an acid catalyst is used. They are permanently fusible or thermoplastic when discharged from the kettle but react with additional formaldehyde to produce a thermosetting resin. This additional formaldehyde is furnished by "hexa" (hexamethylenetetramine). Both one- and two-step resins are used, separately or in combination, in commercial molding materials. Both types are believed to polymerize to similar end products. The two-step scheme is represented in Fig. 34.7,[18] showing the sequences of unit operations and chemical conversions.

[18]Phenolic Resin Process Sidesteps Kettle, *Chem. Eng.* 72 (23) 104 (1965) (flowchart).



In order to produce 100 kg of finished molding compound of a typical kind, the following materials (in kilograms) are required

Phenol	42	H_2SO_4	0.1
Formaldehyde	27	Black dye (Nigrosin)	1.3
Wood flour	52	Ca stearate	0.7
Hexa	3.7		

Fig. 34.7. Flowchart for production of a molding compound of the phenol-formaldehyde type

The phenol and formaldehyde are placed in the reaction kettle with the catalyst (sulfuric acid) and heated 3 or 4 h at a temperature of 140 to 163°C.

During condensation, reaction water is eliminated and forms the upper of two layers. This water of reaction is removed under vacuum without the addition of heat.

The warm, dehydrated, viscous resin is run out of the kettle into shallow trays and allowed to cool and harden. The cooled, brittle resin is crushed and finely ground and becomes the resin binder for molding phenolic resins.

The crushed and ground resin is blended with the activator ("hexa").

Phenolic molding compounds are molded primarily in compression and transfer molds. The powder, mixed with fillers, lubricant, and plasticizers, is further reacted on steam-heated rolls, cooled, and ground. In compression molding the powder is placed in hardened steel molds at a temperature of 132 to 182°C and at pressures from 13.8 to 35 MPa.

In transfer molding the thermosetting material is subjected to heat and pressure in an outside chamber, from which it is forced by means of a plunger into a closed mold where curing takes place.

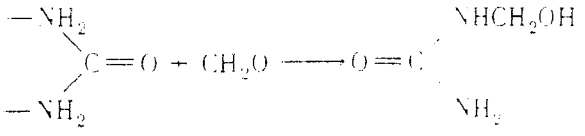
Electronic preheating (in a high-frequency electrostatic field outside the process) of the molding powders as such or in the form of pellets, prior to mold loading, helps achieve a more rapid cure with less pressure, since it promotes the flow of material in the mold cavity.

The final chemical polymerization reaction, or cure, which takes place in the mold to transform the powder into a rigid, infusible shape of the finished article.

Cast phenolics differ from molding compositions in that no pressure is required to make the composition flow. The phenol and formaldehyde with a basic catalyst (usually sodium or potassium hydroxide) are placed in a metal or stainless-steel kettle and heated from the boiling point to as low as 70°C for a period of 10 min to 3 h. Cooling is done by means of water in the jacket during certain phases of the exothermic reaction. At the proper time (removal of about 75 percent of the water formed), while the resin is still hydrophilic, an organic acid

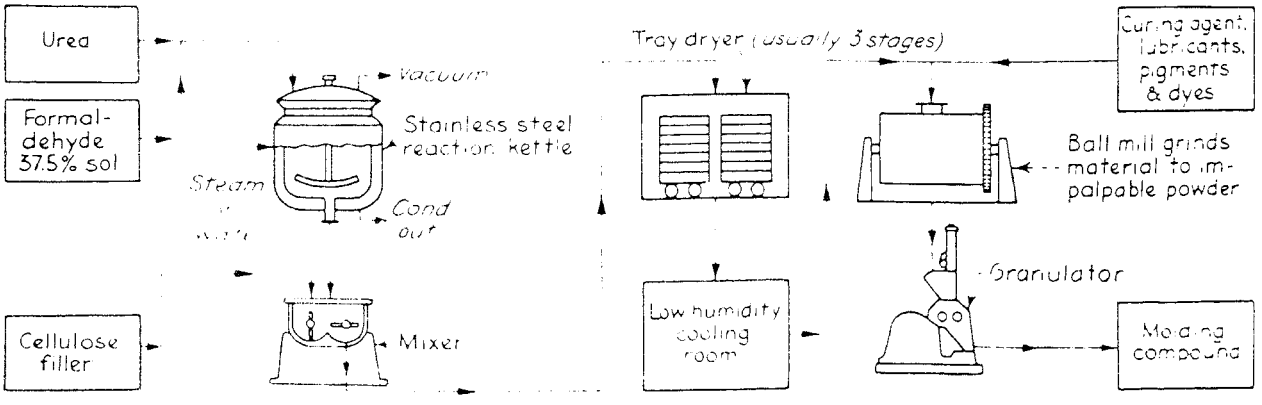
(lactic or maleic acid) is added to neutralize the resin and clarify the color. Before the final dehydration of the resin, plasticizers, pigments, and colors are added to the kettle and mixed with the resin. Dehydration is effected under vacuum at a resin temperature not in excess of 74 to 80°C, and the hot resin is withdrawn and poured into preheated lead molds. The final reaction and hardening take place by curing the resin in the molds at 85°C for periods of 3 to 10 days. The curing ovens are heated with steam under precise temperature control.

AMINO RESINS.[18] Urea-formaldehyde and melamine-formaldehyde condensates are the commercially important amino resins. Other resins in this family utilize sulfonamides, aniline, and thiourea. The simplest condensates are methylolureas and methylolmelamines. A typical low-stage resin is formed when urea (or melamine) is mixed with formaldehyde as shown in Fig. 34.8. The initial reaction of urea (or melamine) with formaldehyde is a simple addition to produce methylol compounds.



Some dimethylol urea ($HOH_2CNH \cdot CO \cdot NHCH_2OH$) is also formed. The mechanism of subsequent intercondensation of the methylol compounds has not been established definitely, but there is evidence for the formation of methylene linkages, $-NH-CH_2-$, or ether bridges, $-NH \cdot CH_2-O-CH_2NH-$, as condensation and curing progress. These water-soluble water-white intermediates are employed in admixture with some form of cellulose before the final reaction and curing to form an infusible, insoluble product. A suitable catalyst and controlled temperature are also needed. Since melamine is not readily soluble in water or formalin at room temperature, it is necessary to heat it to about 80°C to obtain the methylol compounds for melamine-formaldehyde resins

[19]Lichtenberg, MPE, 1981–1982, p. 12; ECT, 3d ed., vol. 2, 1978, pp. 440–469

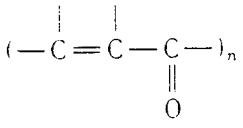


In order to produce 100 kg of molding compound, the following materials (in kilograms) are required

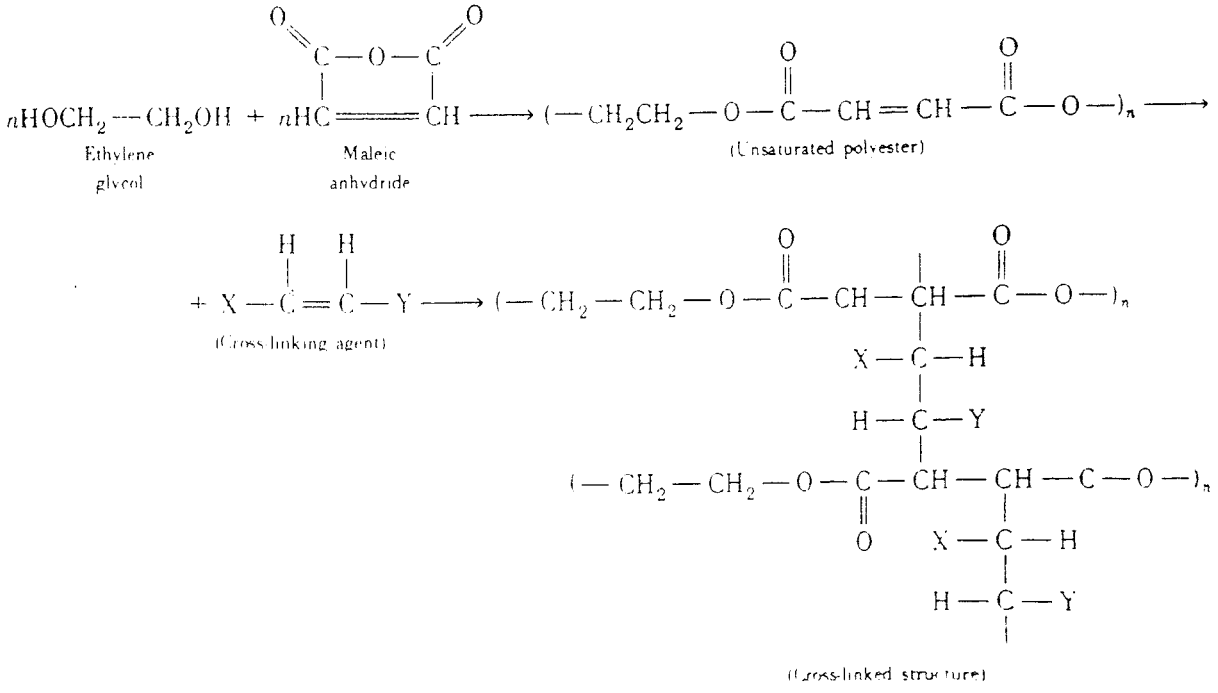
Urea	42	Cellulose filler	40
Formaldehyde	42	Curing agent, lubricant and dye	1.8

Fig. 34.8. Flowchart for the manufacture of a molding compound of the urea-formaldehyde type.

POLYESTER RESINS.[20] Polyester resins are complex esters formed when a difunctional alcohol is reacted with a dibasic acid or anhydride. Since the reaction takes place at both ends of the chain, long molecules are possible and a plurality of ester groups is obtained. Unsaturated polyesters are produced when any of the reactants contain unsaturation, such as



Unsaturated polyesters can be formed in two steps, condensation of the acid and alcohol to form a soluble resin, and then addition of a cross-linking agent to form the thermosetting resin. Typical reactions are:



The condensation reaction is carried out in an insulated stainless-steel or glass-lined kettle. The reactants are usually charged through a manhole (since some of the reactants are solids, i.e., phthalic anhydride, fumaric acid, etc.). An inert gas such as nitrogen is introduced by bubbling it up through the reactants, to keep out oxygen (which may cause discoloration and gelation of the resin).

A mixture is heated to reaction temperature (usually about 200°C) and held from 4 to 20 h as continual mixing takes place. By-product water and the inert gas are removed continuously during the reaction (most of the vaporized glycol is returned by the reflux condenser). When the desired degree of condensation has been attained, generally under vacuum, the product is cooled to prevent premature gelation. The polycondensation product (very viscous) is pumped to the blending tank and mixed with the cross-linking agent (usually 2 to 4 h). The resin is transferred to drums for shipment and storage. For the process flowchart[21] for manufacturing polyester film (Mylar) and polyester fiber (Dacron), see Chap. 35.

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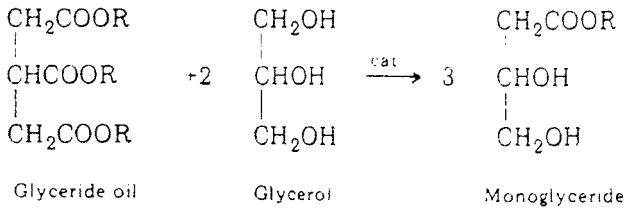
[20]ECT, 3d ed., vol. 18, 1982, pp. 549–574.

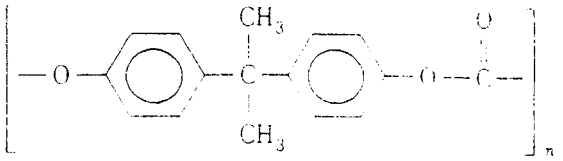
[21]MPE, 1981–1982; ECT, 3d ed., vol. 18, 1982, pp. 549–574.

ALKYD RESINS. The processing equipment (reaction kettle and blending tank) used for unsaturated polyesters can also be used for manufacturing alkyd resins. These are a particular kind of polyester formed by the reaction of polyhydric alcohols and polybasic acids. The most common method of preparation is the "fatty acid" method in which a glyceride oil is catalytically treated with glycerol at 225 to 250°C. The glyceride oil is simultaneously esterified and de-esterified to a monoglyceride.

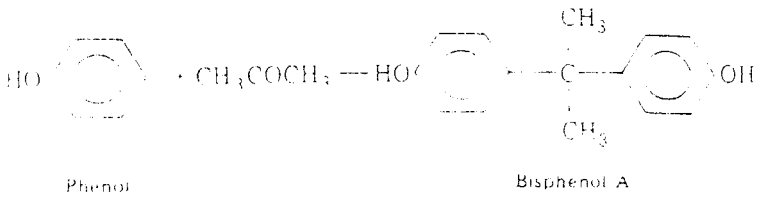


The monoglyceride plus a dibasic acid yields an alkyd resin

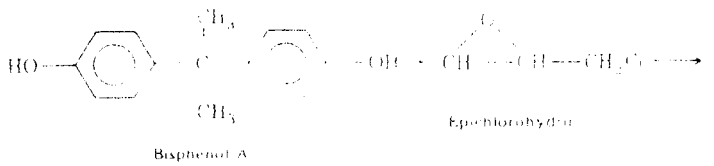
POLYCARBONATES. These resins are a special variety of polyester in which a derivative of carbonic acid is substituted for adipic, phthalic, or other acid and a diphenol is substituted for the more conventional glycols. A number of methods for the preparation of polycarbonates have been described, of which the melt process and the phosgenation process are the most important.[22] Their general formula is

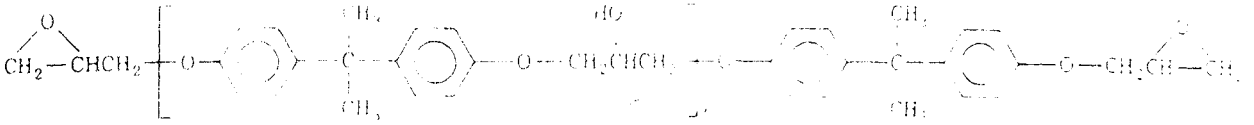


EPOXY RESINS. The most common epoxy resins are formed by the reaction of bisphenol A with epichlorohydrin. Bisphenol A is made from phenol and acetone



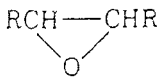
Bisphenol A plus epichlorohydrin gives resins of the following general structure





[22]ECT, 3d ed., vol. 18, 1981, pp. 479–494

If the value of n is low, the resin is liquid; if n is 25 the resin is a hard, tough solid. However, any resin containing one or more epoxide groups is an epoxy resin.[23]



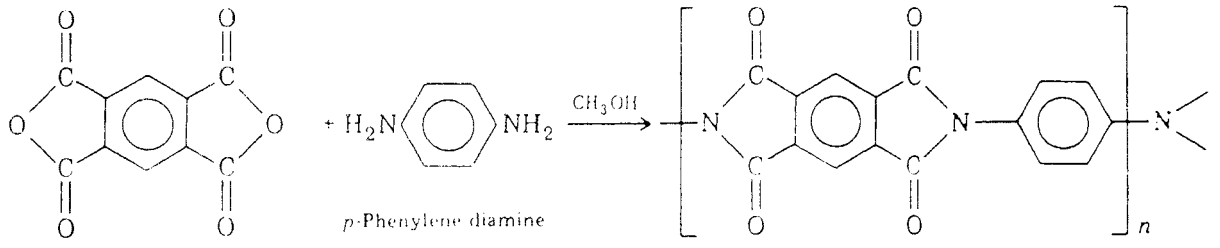
Epoxide group

Most commercial resins are not 100% diepoxides but may contain some other terminal groups such as glycol, phenolic, or chlorohydrin.

The epoxy resins are really intermediates, and must be cured, or cross-linked, to yield a useful resin. Cross-linking occurs by the opening of the epoxide ring caused by addition of a curing agent which must have active hydrogen atoms. Amines, acid anhydrides, and mercaptans are the most usual compounds used as curing agents.

Depending upon molecular weight, epoxy resins have a great many uses ranging from adhesives to can and drum coatings. They have excellent chemical resistance, particularly to alkalies, very low shrinkage on cure, excellent adhesion and electrical insulating properties, and ability to cure over a wide range of temperatures.

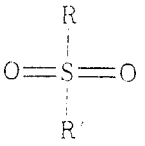
POLYIMIDES. Compounds containing two anhydride groups will react with primary amines or isocyanates to form polyimide polymers which are very stable, linear polymers.



Polymellitic dianhydride

p-Phenylene diamine

POLYSULFONES.[24] These are both aliphatic and aromatic polymers that contain the structural unit



They are resistant to high temperatures and are ultrastable. Their resistance to autoclave sterilization makes them useful for medical instruments and trays. Other uses are microwave cookware, coffee decanters, and corrosion-resistant piping. A typical preparation is the reaction of disodium bisphenol A with 4,4'-dichlorodiphenylsulfone.

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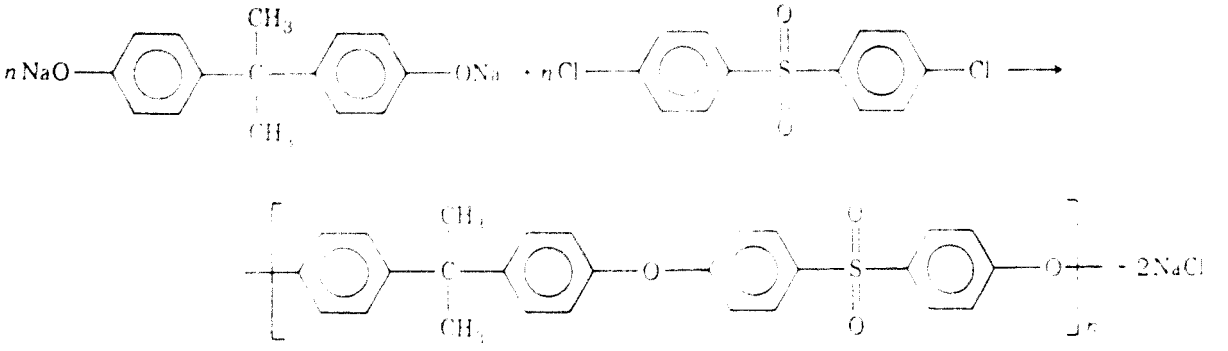
[23]Bauer, The Versatile Epoxies, *CHEMTECH* **10** (11) 692 (1980).

[24]ECT, 3d ed., vol. 18, 1982, p. 832; Steinberg, Substituting Polyketones and Polysulfones for Polyethylene, *Chem. Eng. Prog.* **72** (9) 75 (1976); Fried, Polymer Technology, Part I, *Plast. Eng.* 38 (6) 49 (1982).



Addition Polymerization

POLYOLEFINS. *Polyethylene* was the first and still is the largest in production of polyolefin plastics. Imperial Chemical Industries (ICI) of England inadvertently discovered the white waxy solid in 1933 while attempting to react ethylene with benzaldehyde in an autoclave. The original ICI process operated at 50 to 300 MPa. This was one of the highest-pressure processes employed in the organic chemical industry.

Two types of polyethylene have been available.[25] High-density polyethylene (HDPE), produced by low-pressure methods, is used mainly for blow-molded containers and injection-molded articles and pipe. Low-density polyethylene (LDPE), produced by high-pressure methods, is used mainly for plastic films. Within the past five years new processes for producing low-density polyethylene at lower pressures have been introduced. These new low-density polymers have a small amount of α-olefin as comonomer and are called linear low-density polyethylene (LLDPE). Union Carbide's process uses butene, Dow and DuPont use octene, and Phillips uses hexene. The structural differences between the high- and low-density polyethylenes are in the structure of the polymer chain. Low-density polyethylene's chain is highly branched with both short- and long-chain branches, and the high-density material has very few side chains. The new LLDPE contains short side chains that are spaced uniformly and periodically on the long backbone chain. HDPE has a density greater than 0.960 g/cm^3. LDPE's density ranges from 0.910 to 0.940, and the commercial LLDPE density usually ranges between 0.918 and 0.940.

Figure 34.9 shows a high-pressure process using oxygen or peroxides for catalysts. Polyethylene manufacture requires high-purity ethylene, and the first steps involve the demethanizer, where a mixture of methane-ethylene is removed and recycled. The feed passes to a deethanizer, where 99.8% ethylene is taken overhead and the bottoms, ethane, recycled. A free-radical yielding catalyst, such as a peroxide, is added to the high-purity ethylene, compressed to operating pressure (150 MPa), and fed to the tubular reactor which is maintained at 190°C. The reaction takes place in solution. Conversion per pass is about 30 percent. The effluent from the reactor passes to a high-pressure separator in which the unconverted ethylene is removed and recycled. The polyethylene is extruded, pelletized, and dried.

One of the low-pressure processes to produce LLDPE is that of Union Carbide's Unipol process as shown in Figure 34.10.[26] The purified ethylene and 1-butene for comonomer are fed

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[25]Paschke, The Outlook for High-Density Polyolefin, *Chem. Eng. Prog.* **76** (1): 74 (1980); LDPE Goes Low Pressure, *Chem. Eng.* **85** (1): 25 (1978); ECT 3d ed., vol. 16, 1981, p. 385; *Chem. Eng.* **89** (25): 17 (1982).

[26]New Route to Low-Density Polyethylene, *Chem. Eng.* **86** (26): 80 (1979); A Step Up for LLDPE Know-How, *Chem. Week* **130** (13): 11 (1982).

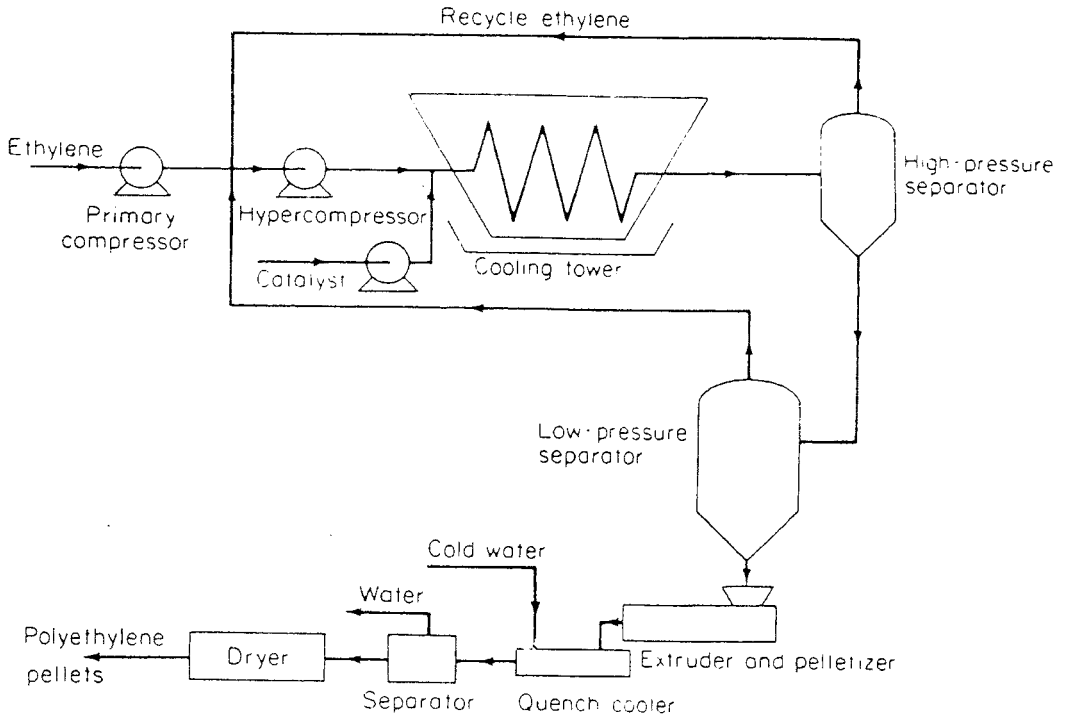

Fig. 34.9. Low-density polyethylene by high-pressure processing.

to the fluid-bed reactor which is maintained at 100°C and 0.7 to 2 MPa. The reaction takes place in the gas phase. The fluidized bed is composed of granular polyethylene polymer which has been previously produced by the reaction. The unreacted ethylene passes out the top of the reactor and then is compressed, cooled, and returned to the reactor. The polyethylene is removed as dry, free-flowing granules from the bottom of the reactor through a gas-lock chamber. The product is purged with nitrogen and is ready for storage. The average time of the polymer in the reactor is 3 to 5 h and the particles grow during this time to about 1 000 μm.

Polypropylene is used for injection molding for toys, automobile parts, and appliances (40 percent), fibers (35 percent), and films (10 percent) and is made by several processes similar to those used for polyethylene. The development of more active catalysts has eliminated pro-

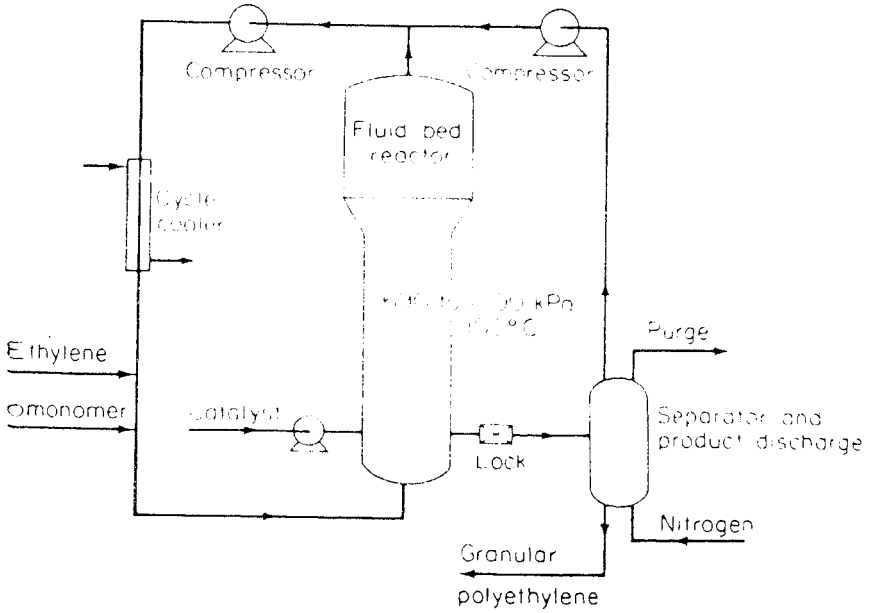

Fig. 34.10. High-density polyethylene by low-pressure resins.

cess steps and cut costs and energy requirements. The basic catalyst, used for the past 20 years, is titanium trichloride with aluminum chloride present as a solid solution in the titanium trichloride matrix. It is made by treating aluminum with titanium tetrachloride.

$$Al + 3TiCl_4 \rightarrow AlCl_3 \cdot (TiCl_3)_3$$

Various improvements have been made, such as by addition of a third component, such as diethyl or triethyl aluminum chloride, to modify the crystal structure and by making a supported catalyst. Other improvements have been made by closely guarded trade-secret means. Typical processing schemes have been described.[27] In the United States polypropylene is produced by solution polymerization (Eastman), hydrocarbon slurry (Hercules, Solvay, Amoco, Eastman), propylene slurry (Phillips, Dart Industries), and in the gas phase (Northern Petrochemicals). The two new processes are the gas-phase and propylene slurry.

The propylene slurry process does not require any other hydrocarbon, which simplifies feedstock inventory and recycle systems. The reaction takes place in a reactor which consists of a large-diameter pipe assembled in a loop configuration. The propylene, catalyst, and cocatalyst are fed to the loop continuously. The slurry of polypropylene in liquid propylene is discharged continuously to a vessel where polymerization terminating agents are added. Washing with liquid propylene and flashing off the propylene yields a powder which is extruded and pelletized.

An interesting battle was waged over the patent rights to crystalline polypropylene. In contention were DuPont, Montedison, Standard Oil of Indiana, and Phillips Petroleum. Originally Montedison had a patent dated February 6, 1973, but in 1980 the courts declared that Montedison had committed fraud during a patent examiner's meeting, and awarded prior invention rights to Phillips. The stakes were, and are, millions of dollars in licenses and royalties. In 1982 the U.S. Supreme Court upheld the lower court and awarded patent rights to Phillips who will now be issued a patent.[28]

VINYL RESINS.[29] The polyvinyl resins are synthetic materials made from compounds having a vinyl ($-CH=CH_2$) group. The most important members of this class are polyvinyl acetate, polyvinyl chloride, polyvinyl alcohol, and polyvinyl acetals and copolymers of vinyl chloride with vinyl acetate, and vinylidene chloride. See Fig. 34.11 for a simplified flowchart for vinyl resins. *Polyvinyl acetate* may be prepared by introducing a benzene solution of vinyl acetate containing the desired catalyst into a jacketed vessel. At a temperature of about 72°C, the mixture boils and the vapors are condensed and returned to the kettle. After about 5 h at a gentle boil, the reaction mixture is run to a still, and the solvent and unchanged vinyl acetate are removed by steam distillation. The molten resin is then either run into drums, where it solidifies, or extruded into rods and sliced into flakes. Polyvinyl acetate is used primarily in paints and adhesives. About 20 percent of the vinyl acetate produced is used to make polyvinyl alcohol.

The largest branch of the vinyl family is *polyvinyl chloride* (PVC). The popularity of PVC is due to its excellent physical properties, its ability to be compounded for a wide range of applications, its ease of processing, and its relatively low cost.

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[27]Short, Polypropylene: Processes, Catalysis, Economics, *CHEMTECH* **11** (4): 238 (1981); Cipriani and Trischman, New Catalyst Cuts Polypropylene Costs and Energy Requirements, *Chem. Eng.* **88** (8): 80 (1981); ECT, 3d ed., vol. 16, 1981, pp. 453–469.

[28]*Plast. World* **40** (7): 10 (1982).

[29]MPE, 1981–1982; *Hydrocarbon Process.* **60** (11): 233 (1981).

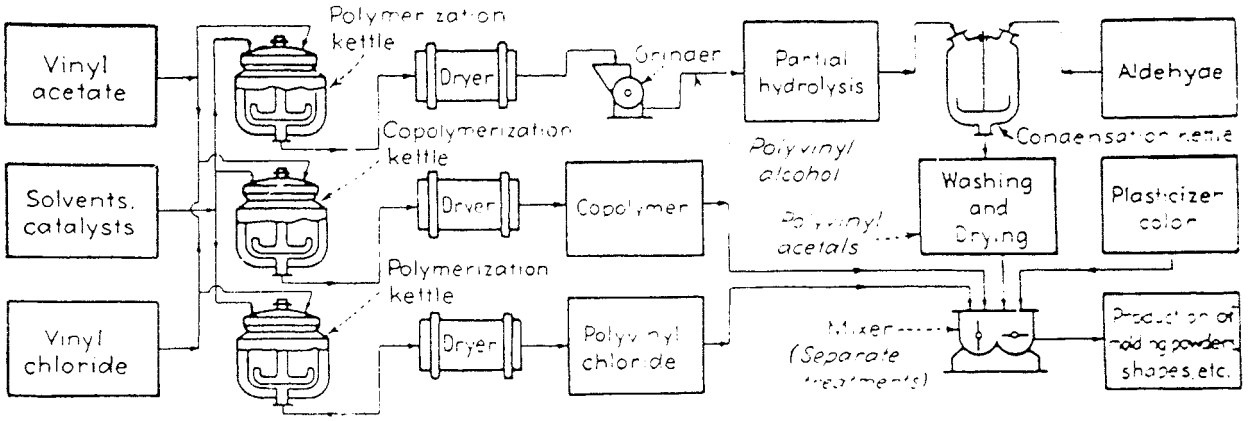


Fig. 34.11. Flowchart for polyvinyl resin manufacture.

The liquid monomer is formed into tiny globules by vigorous stirring in water containing a suspending agent. A typical recipe lists 100 parts of water, 100 parts of liquid vinyl chloride, 1 part of a persulfate catalyst, and 1.5 parts of an emulsifier such as sodium lauryl sulfate. The autoclave operates at 40 to 45°C for 72 h to give a yield of 90 percent of polymer with a particle size of 0.1 to 1.0 μm. Recovery of these particles may be accomplished by spray-drying, or by coagulation by acid addition. A PVC compound can be tailor-made to achieve whatever balance of properties is desired by using plasticizers, stabilizers, lubricants, and fillers. Almost 40 percent of the U.S. production is used to manufacture construction pipe.

Copolymers of vinyl chloride and other vinyls retain the toughness and chemical resistance of PVC but are more flexible. Studies of these copolymers were carried out because of the practical limitations (high molding temperature, poor heat stability, etc.) encountered with PVC in its early development. The monomers of both acetate and chloride are mixed with a solvent and catalyst and polymerized in an autoclave to yield a copolymer which may be represented in part as follows:

$$\cdots CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-\cdots$$
$$\quad Cl \qquad\quad Cl \qquad\quad O{-}OCCH_3$$

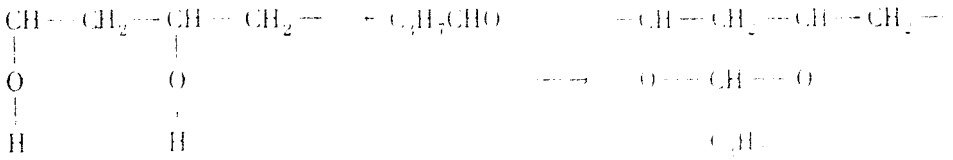
Although the acetate-chloride ratio can be varied over wide limits to give resinous products suitable for a great variety of applications, the more important copolymers usually contain a preponderance of chloride.

Vinyl Alcohol Resins. These resins are made from polyvinyl acetate which is first reacted with alcohol to yield polyvinyl alcohol and then condensed with aldehydes to give a group of resins. The polyvinyl acetate is reacted with alcohol under controlled conditions with a trace of either acid or alkali which replaces the acetyl groups with hydroxyl groups to yield polyvinyl alcohol:

$$\cdots CH-CH_2-CH-CH_2-\cdots + ROH \longrightarrow \cdots CH-CH_2-CH-CH_2-\cdots + CH_3CO_2R$$
$$\quad O{-}OCCH_3 \qquad\quad O{-}OCCH_3 \qquad\qquad\qquad OH \qquad\quad OH$$

This method of preparation is used because polyvinyl alcohol cannot be prepared by direct polymerization since the monomer vinyl alcohol is an unknown compound and exists as the enol form of acetaldehyde (CH_3CHO). Polyvinyl alcohol is a unique plastic because it is plas-

ticized by water and is completely soluble in an excess of water. Polyvinyl alcohol reacts with an aldehyde under the influence of heat and in the presence of an acid catalyst such as sulfuric or hydrochloric acid, and the result is a typical acetal. Polyvinyl butyral is formed as follows:



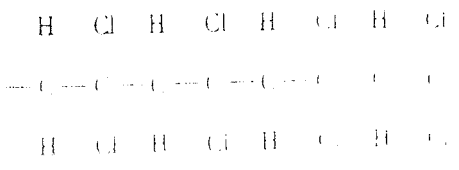
The corresponding formal and acetal are

Formal

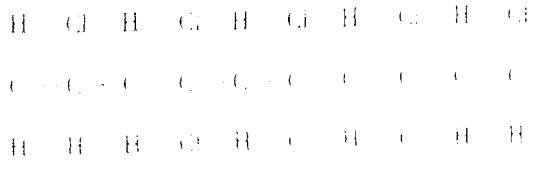
In actual commercial production, the hydrolysis and condensation reactions are never carried to completion because it has been found that the presence of residual acetyl and hydroxyl groups gives the resins better properties.

Polyvinyl butyral is usually extruded as a sheet for the interlayer for safety glass. Some polyvinyl acetals can be compression-molded at temperatures from 100 to 130°C and injection-molded at temperatures from 170 to 190°C. Polyvinyl formals can be molded by either compression or injection, depending upon the softening point.

Vinylidene Resins. This class of resins was introduced in 1940 and is formed by the polymerization of the monomeric vinylidene chloride, $CH_2=CCl_2$, or vinylidene fluoride. These resins may be represented as:



or the monomer may be copolymerized with vinyl chloride to give a new product represented as:



The resins formed by copolymerization range from a flexible material having a softening point of about 70°C to a hard, thermoplastic solid with a softening point of 150°C. Their higher softening point indicates a greater degree of crystalline character. If the fibrous crystals are not oriented, the vinylidene chloride has a tensile strength of 55 MPa, which is an ordinary value. If the crystals are oriented by drawing, however, the tensile strength may be increased to about 410 MPa. These resins may be fabricated by compression or injection

molding or extrusion with the use of specially developed techniques and equipment to obtain accurate control of properties and shape.

STYRENE RESINS.[30] Monomeric styrene (Chap. 36) is made by the pyrolysis-dehydrogenation of ethylbenzene, which is synthesized from ethylene and benzene. The factors that affect polymerization of the monomer are the temperature and purity of the styrene. Polymerization at moderate temperatures without catalysts produces resins of high average molecular weight, which impart high viscosity to their solutions. If the temperature is increased and catalysts such as benzoyl peroxide, oxygen, or stannic chloride are added, the average molecular weight and viscosity tend to decrease. Styrene of 99.5% purity, when heated to 80 to 85°C in a stainless-steel kettle, polymerizes to a 35 or 40 percent conversion in 40 to 60 h. The viscous solution is passed down a tower, with zones of increasing temperature up to 200°C, to strip off the unconverted monomer and to take off the polymer in a molten state. The extruded product is cooled and granulated. A blend of acrylonitrile-butadiene rubber with acrylonitrile-styrene resins produces ABS plastics.

Another variation of polystyrene is a recently introduced poly *p*-methyl styrene, PMS. The *p*-methyl styrene is prepared from toluene and ethylene, and it is claimed that this is cheaper to produce than styrene. Superior properties are another plus for the PMS over polystyrene[31]

ACRYLIC RESINS AND PLASTICS.[32] The methyl, ethyl, and butyl esters of acrylic and methacrylic acids are polymerized under the influence of heat, light, and peroxides. The polymerization reaction is exothermic and may be carried out in bulk for castings, or by emulsion, or in solution. The molecular weight decreases as the temperature and catalyst concentration are increased. The polymers are noncrystalline and thus very clear. Such resins are widely used because of their clarity, brilliance, ease of forming, and light weight. They have excellent optical properties and are used for camera, instrument, and spectacle lenses. Because of their excellent dielectric strength they are often used for high-voltage line spacers and cable clamps. Emulsions are widely applied as textile finishes and paints.

Alloying and Blending[33]

The properties of many plastics can be greatly modified by blending or alloying two or more polymers. The terms are often used interchangeably but technically blends are mixtures that are not fully compatible, and alloys are mixtures that are fully compatible such as polyphenylene oxide and polystyrene. The blends appear as separate phases when viewed under a microscope. These combinations are taking over an increasing share of the market because it is much easier to develop desirable properties by mixing known plastics than by creating new ones.

One of the problems associated with blends and alloys is how to make the components adhere together. One approach is to introduce a compatibilizer which creates interpenetrating polymer networks by providing a physical link between semicompatible materials. Most compatibilizers are block copolymers and they produce an interwoven matrix of physical

[30] *Mod. Plast.* 52, 6, 16 (1975); *Hydrocarbon Proc.*, 58, 9, 185, (1979); MPE, 1982–1983.

[31] A Better Styrene Goes Commercial, *Chem. Week*, 130, 7, 42, 1982.

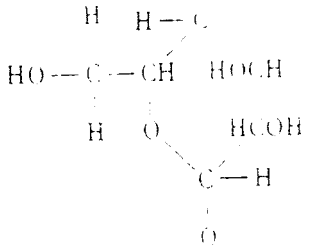
[32] DuBois and John, *Plastics*, 6th ed., Van Nostrand Reinhold, New York, 1981.

[33] Polymer Alloys, *Chem. Week*, 132, 9, 72, 1983.

inseparable, but chemically distinct, polymers. Manufacturers are very secretive about the polymers they are using for blends and alloys and are especially protective of the nature of the compatibilizers. Some of the major polymer alloys are polyphenylene oxide/polystyrene (Noryl), acrylonitrile-butadiene-styrene (ABS)/polycarbonate (Fiberite), polyvinyl chloride/ABS (Cycoloy), and polycarbonate (PC)/polyethylene terephthalate (PET) (Xerox).

Natural Products

CELLULOSE DERIVATIVES.[34] Cellulose is generally pictured as being composed of a chain of glucosidic units represented by the formula



Long chains may contain 3000 to 3500 units. These elongated chains and the reactions of the cellulosic polyhydric alcohol are responsible for the formation of tough, flexible, cellulosic plastics. The properties of the cellulose derivatives depend upon the substituent groups, the amount of substitution, the type of pretreatment, and the degree of degradation of the long chains into shorter lengths.

CELLULOSE NITRATE. This was the first synthetic plastic. Flowcharts for the production of cellulose nitrates are given in Fig. 22.2. Fully nitrated cellulose is unsuited for a plastic base because of its extremely flammable character. Hence, a partly nitrated product is made. Products containing 11% nitrogen are used for plastics, 12% nitrogen for lacquers, and the fully nitrated, or 13% nitrogen-containing, material is used for explosives. The cellulose nitrate is placed in large kneading mixers with solvents and plasticizers and thoroughly mixed. The standard plasticizer is camphor, first used by Hyatt in 1868. The compounded mixture is strained under hydraulic pressure and mixed on rolls with coloring agents. The material is pressed into blocks. Finally, the plastic is made into sheets, strips, rods, or tubes, seasoned to remove the residual solvent, and polished by pressing under low heat. This plastic possesses excellent workability, water resistance, and toughness. Its chief disadvantage is the ease with which it burns. It also discolors and becomes brittle on aging. The tradename is Celluloid.

CELLULOSE ACETATE. Fully acetylated cellulose is partly hydrolyzed to give an acetone-soluble product, which is usually between the di- and tri-ester. The esters are mixed with plasticizers, dyes, and pigments and processed in various ways, depending upon the form of plastic desired. The important properties of cellulose acetate include mechanical strength, impact resistance, transparency, colorability, fabricating versatility, moldability, and high dielectric strength.

Cellulose acetate is moldable, in contrast to cellulose nitrate which is not. It, however, has

[34]ECT, 3d ed., vol. 3, 1979, pp. 119–162

poor resistance to moisture. To overcome this disadvantage, a mixed acetate-butyrate is produced by treating the cotton linters with a mixture of butyric acid, acetic acid, and acetic anhydride. The plastics made from this material have better moisture resistance and better dimensional stability than cellulose acetate. They also have excellent weathering resistance, high impact strength, availability in colors, and improved finish.

ETHYL CELLULOSE PLASTICS. Ethyl cellulose is a cellulose ether in which ethyl groups have replaced the hydrogen of the hydroxyl groups. Commercial ethyl cellulose contains between 2.4 and 2.5 ethoxy groups per glucoside unit of the cellulose chain. The ethers are made by treating cellulose, such as wood pulp or cotton linters, with a 50% solution of sodium hydroxide. Alkali cellulose formed is alkylated with ethyl chloride or ethyl sulfate. The alkylation must be carried out under carefully controlled conditions to prevent degradation of the cellulose chain and destruction of the alkylating agent. After the reaction is complete, the excess reagents are easily washed out. The ether is purified by washing it free of soluble materials. Ethyl cellulose plastics may be molded in any manner or machined. Some of the outstanding properties are unusually good low-temperature flexibility and toughness, wide range of compatibility, stability to heat, thermoplasticity, and electrical resistance. Methyl cellulose is prepared by a process almost identical with that for ethyl cellulose, substituting methyl chloride or sulfate for the corresponding ethyl derivative. Water solubility, plus the ability to produce viscous solutions, have made it useful for a thickening agent in the textile, food, and adhesives industries.

SHELLAC.[35] Shellac is obtained from a resinous material secreted by an insect, *Kerria lacca*, which is native to India. The insect produces raw lac from glands located in its skin. The resin is a solid solution of several chemical compounds having similar structures. The lac consists of two materials, a hard and a soft resin. Shellac is a unique plastic resin because it has properties of both thermoplastic and thermosetting resins. Heat curing increases its mechanical and electrical strength. The resin is compatible with phenolic resins, so that a wide variety of molding compositions can be made. Compositions are softened on steam tables at 107 to 121°C. They are molded by compression molding at temperatures from 121 to 135°C and pressures from 6.9 to 24 MPa. The molds must be cooled to 32 to 40°C before the pressure is released. Injection molding at 110°C can be carried out in a 1- or 2-min cycle for many pieces. Some noteworthy properties of shellac compositions are low dielectric constant, high dielectric strength, arcing resistance, adhesion, hardness, high gloss, resilience, low thermal conductivity, ease of molding, ability to wet fillers, and oil resistance when cured. These compositions find use in protective coatings, adhesives, and electrical insulation.

LIGNIN PLASTICS.[36] The lignin bond of woody material is released by the action of high-pressure steam which activates the lignin so that it can be used as a plastic binder. Wood chips are charged into suitable containers and treated with steam at pressures up to 8.3 MPa for a period of seconds. Normally the time cycle, including the filling and emptying of these containers, is about 1 min. In this time the lignin is softened by the sudden high temperature. When the chips are suddenly released to atmospheric pressure, they are exploded by the high internal pressure into a mass of fibers and fiber bundles which still contain a natural coating of lignin. These fibers are formed into mats under pressures from 10 350 to 17 200 kPa and

[35]EPST, vol. 12, p. 419.

[36]ECT, 3d ed., vol. 14, 1979, p. 294.

at a temperature of 135 to 196°C. The product is usually cured at a pressure of 10,350 kPa and a temperature of 175°C. The only plasticizer needed is about 4% moisture, which is present at usual humidities. The curing is very rapid.

PROTEIN DERIVATIVES. Historically, the industrial use of proteins is quite old. Animal glues have been in use since early Egyptian civilization, yet the supply of such glues was limited until recent times because of inadequate refrigeration and transportation facilities. See Adhesives, Chap. 25. Vegetable proteins, developed along with the soybean in the 1930s, were followed by the industrial use of zein in the 1940s. Protein plastic compositions are hygroscopic and are accordingly affected by atmospheric moisture changes. The absorption of water causes severe warping in sizes larger than 26 cm^2. The soft, uncured plastic may be molded but requires hardening in formaldehyde solution and, since thinner sections harden sooner than the thicker parts, the resulting internal stresses and strains cause severe warping. At present, protein derivatives find extensive use as glues, adhesives, and paper coatings.

Laminates and Foams

A laminated material is formed from layers of material bonded together. Laminated plastics are made largely from the thermosetting class of resins (melamine, epoxy, unsaturated polyester, silicone, and, most frequently, phenolics) and have fibrous fillers such as glass, carbon, metal, and some polymers. See Table 34.9 for the various fibers commonly used. The resin is dissolved in a suitable solvent, such as alcohol or water, with which the filler is impregnated or coated. One method of impregnating utilizes adjustable rollers or a doctor blade to control the amount of resin left on fibers after dipping in a bath. Another technique controls the concentration of the resin in the dipping tank. A third technique meters the resin applied to the fibers as they are passed through a drying oven and partial polymerization takes place. Final cure is usually accomplished in presses or molds. This curing time varies with the thickness and type of material used but high pressures of approximately 6900 to 17,200 kPa are employed with temperatures from 130 to 175°C.

Foamed[37] or cellular plastics are available in two types, closed cell and open cell. In the closed cell, each cell is completely enclosed, and in the open cell, the cells are interconnected as in a sponge. These foams are formed by adding blowing or foaming agents to the resin and then heating to cause the additives to foam, or by gaseous by-products of the polymerization reaction. Many times a low boiling liquid, such as a fluorocarbon, is used as the blowing agent. The common foaming agents are compounds which give off carbon dioxide or nitrogen gases. Azodicarbonamide, which gives off CO, N_2, and NH_3 on heating, is often used. The polymer may be foamed prior to fabrication or during the extrusion process. The common foams are polystyrene and polyurethane, but all thermoplastics can be foamed.

Flexible, semirigid, and rigid foams in densities ranging from 1.6 to 960 kg m^3 can be made. The major uses for flexible foams, density below 100 kg/m^3, are for bedding, furniture, and automotive applications. The rigid foams are generally used as insulation. These may be applied by foaming in place, or by using cut slab material already foamed. Heavy-duty structural foams are formed by fusing solid skins of plastics to a rigid cellular core.

[37]DuBois and John, op. cit; Driver, op. cit.

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Chapter 5

Rubber Industries

Rubber has become a material of tremendous economic and strategic importance. In the United States, the per capita consumption of rubber is approximately 16.8 kg; in India it is scarcely 0.22 kg. Transportation, the chemical, electrical, and electronic industries, and the space effort are all major consumers of rubber. When supplies of natural rubber were shut off because of Japan's invasion of rubber-producing areas early in World War II, the United States built up a synthetic rubber industry which has continued to expand enormously, so that at the present time 88 percent of the rubber consumed in the United States is of synthetic origin. The rubber industry involves the production of monomers or raw materials for synthetic rubbers, the various rubbers themselves, the importation of natural rubber, the production of rubber chemicals, and finally the fabrication of rubber products.

HISTORICAL. Columbus found the natives of the West Indies playing games with rubber balls. Rubber articles have been recovered from the sacred well of the Maya in Yucatan. Rubber, as we know it, is a product of the Americas but has achieved its greatest growth by transplantation to the Far East. The name "rubber" was apparently given by Priestley, the discoverer of oxygen, who first observed the ability of the material to "rub out" a pencil mark. Rubberlike materials resulted from mere efforts to purify and keep such materials as styrene, butadiene, and the isoprene produced from the destructive distillation of natural rubber; thus early attempts were made to produce synthetic rubber. By the outbreak of World War I, inferior grades of rubber were being produced from dimethylbutadiene in Germany and in Russia. Extensive research during the 1920 to 1930 period led to discovery of the emulsion copolymerization of butadiene and styrene, and of butadiene and acrylonitrile.

Goodyear is credited with the discovery of the cure, or vulcanization, of rubber with sulfur in 1839. This overcame the natural tackiness of rubber and commercialized it. Since then it has been found that many substances affect the rate of this reaction and that some subsidiary materials modify or improve the compound, making it possible to shape or fabricate an article which is then fixed into its final form by the curing reaction. The historical occurrence of most significance was the curtailment of natural rubber importation caused by Japanese invasions in 1941. This stimulated both research and the manufacture of various synthetic rubbers in the years following.

ECONOMICS. Table 36.1 shows the consumption of natural and synthetic rubber in the United States over a 19-year period. It can be clearly seen that synthetic rubber supplies the largest portion of the market although it has not completely supplanted natural rubber. The prices of natural rubber and synthetic rubber have fluctuated over the years because of wars, inflation, and other nonnatural causes. In 1982 the list price of the most widely used synthetic, SBR, was $1.26 per kilogram, compared with 88 cents per kilogram in 1979. The price of natural rubber has fluctuated widely from 45 cents per kilogram in 1945, to one dollar in

Table 36.1 Total U.S. Consumption of Natural and Synthetic Rubber (in thousands of metric tons)

Year	Natural	Synthetic	Total
1960	756	1079	1835
1965	786	1540	2326
1970	759	1918	2677
1975	250	2706	2956
1979	436	3409	3845

SOURCE: *Statistical Abstract on the United States*, U.S. Dept. of Commerce, 1981.

1952, to $1.60 in 1980. Table 36.2 shows the costs of synthetic rubber relative to the cost of oil for a period of years. Although the cost of oil has increased tenfold, the cost of the synthetic rubbers have only increased by a factor of about three.

NATURAL RUBBER

Dandelion, guayule, goldenrod, osage orange, and numerous other plants have been proposed as sources of rubber, but none has proved to be as successful as the latex-producing tree *Hevea brasiliensis*, a native of South America, and the collection of balata and chicle from other species of trees. Natural rubber has become established on plantations in Malaya, Indonesia, Liberia, and their neighbors, probably because of freedom from insect and fungus diseases which beset the tree in its native areas in the Americas. Trees require approximately 7 years to reach bearing age and may then continue to yield for a number of years. Yields were increased by the selection of improved stock to produce approximately 2400 kg/ha-year during World War II. More than 3000 kg/ha-year can be obtained from the improved types of trees now being planted. The collection and processing of the latex requires considerable labor, and the crop is adaptable to the densely populated areas of the Far East and Africa, but has not proved to be attractive in this hemisphere.

Table 36.2 Cost of Synthetic Rubber Relative to the Cost of Oil

Year	Synthetic Rubber	OPEC Crude Oil $/m^3
1967*	100	—
1973	102	0.52
1975	146	1.75
1976	156	1.87
1977	166	2.04
1978	179	2.04
1979	208	2.95
1980	252	4.89
1981	290	5.37

*1967 = 100.

SOURCE: *U.S. Industrial Outlook*, 1982.

Latex is obtained by tapping the tree in such a manner as to allow the liquid to accumulate in small cups, which must be collected frequently to avoid putrefaction or contamination. The latex is carried to collection stations where it is strained and a preservative (NH_3) added. The rubber is separated by a process known as coagulation, which occurs when various acids or salts are added and the rubber separates from the liquid as a white, doughlike mass, which is then milled and sheeted to remove contaminants and to allow drying. A newer method is to form the coagulated latex into granules by cutting with rotating knives or by shear between two rollers running at different speeds. The granules are dried in mechanical dryers in hours, instead of the days that air or wood-smoke dryers required. Either the dried sheet or granules are compressed into bales weighing 33 kg. Some natural rubber is marketed as a latex, concentrated after stabilization with ammonia and centrifugation to about 60% rubber.

Rubber must be softened before it can be compounded with various necessary additives. This may be done with a two-roll mill whose rolls revolve at different speeds, or a mixer in which an eccentrically shaped rotor works the rubber against the walls of the mixer. After softening, the compounding materials, such as carbon black (for filler), sulfur or sulfur compounds (for vulcanization), vulcanizing acelerator, protective antioxidant, and oil, are mixed either in the same mixer or rolls. Only the smallest factories use roll mixers. The mixers are very large and can only handle a small amount of rubber at one time. A typical mixer may be two stories high, and only handles a batch of about 250 kg.

After mixing, the rubber is shaped into the desired product by extruding, or molding, and then vulcanized. Vulcanization leads to a cross-linked thermoset polymer that cannot be softened or melted by reheating to the original melting point. It is important to carefully control the heat of vulcanization (140°C or more) to obtain optimum properties in the finished rubber. As the vulcanization is a chemical reaction, its speed increases with temperature and care must be taken to ensure that it does not take place prematurely.[1]

Natural rubber (NR) is *cis*-1,4-polyisoprene and, when stretched, the molecules crystallize producing a superior form of reinforcement. Structural prerequisites of both natural and synthetic rubbers are long threadlike molecules. Their characteristic property of reversible extensibility results from the randomly coiled arrangement of the long polymer chains. When extended, the chains are distorted but, like a spring, they revert to the kinked arrangement upon removal of the stress. NR contains 6 to 8% nonrubber materials and has an outstanding heat-buildup resistance. Table 36.3 shows the monomers and polymers or copolymers of various rubbers.

SYNTHETIC RUBBER[2]

Synthetic rubbers have been classified into vulcanizable and nonvulcanizable and also by the chemical composition of the polymer chain. Table 36.4 shows the various classes and types, together with the accepted abbreviations. The most widely used synthetic rubber is SBR as shown in Table 36.5. Other commonly used elastomers are polybutadiene, polyethylene-propylene, butyl rubber, neoprene, nitrile rubbers, and polyisoprene.

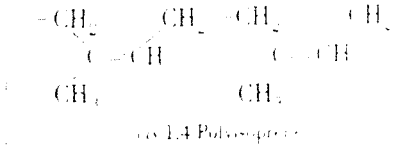
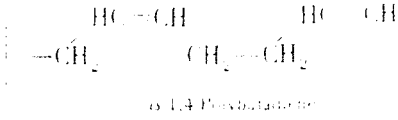
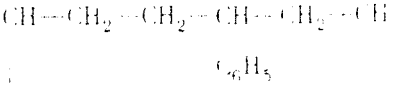
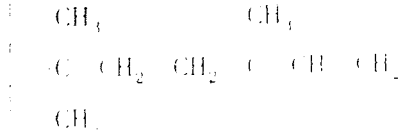
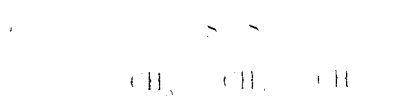
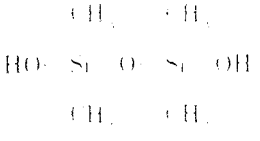
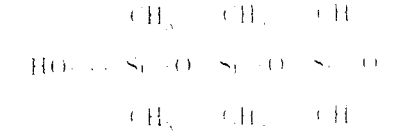
MONOMER PRODUCTION. *Butadiene* production is about 1.8×10^6 t/year.[2a] Most of it is obtained as a coproduct of the steam cracking of petroleum for ethylene manufacture. Dehy-

[1]Allen, *Natural Rubber and the Synthetics*, Wiley, New York, 1972.

[2]See Perry, table 23-13, for physical properties of natural and synthetic rubbers.

[2a]t = 1000 kg.

Table 36.3 Monomers and Polymers or Copolymers of Rubbers

Monomer	Polymer or Copolymer Unit	Rubber
Isoprene, Hevea latex	 cis-1,4-Polyisoprene	Natural, NR 5,000 isoprene units
Isoprene $CH_2{=}C(CH_3){-}CH{=}CH_2$		Synthetic polyisoprene, IR
Butadiene $CH_2{=}CHCH{=}CH_2$	 cis-1,4-Polybutadiene	
Styrene $CH_2{=}CH(C_6H_5)$		
Butadiene-styrene		SBR (GR-S)
Acrylonitrile $CH_2{=}CHCN$		
Butadiene-acrylonitrile		Nitrile, NBR
Chloroprene $CH_2{=}CCl{-}CH{=}CH_2$		Neoprene, CR
Isobutylene-isoprene		Butyl, IIR
Sodium tetrasulfide-ethylene dichloride		Thiokol A
Dimethylsiloxane 		Silicone R

drogenation of butane or butenes is an alternate route used when supplies are short and may be either a one- or two-step operation. In the one-step or Houdry process, Figs. 36.1 and 36.2, *n*-butane is the feedstock, the catalyst is aluminum and chromium oxides, and the yield of 1,4-butadiene is 57 to 63 percent. The butadiene is not pure enough for polymerization, so it is purified by absorption from the reaction product with cuprous ammonium acetate. The two-stage process first converts the *n*-butane to *n*-butenes, and then using an oxidation-dehydrogenation catalyst plus compressed air or steam, the *n*-butenes are converted to 1,4-butadiene.

Table 36.4 Classification of Rubbers

Class I. Elastomers
A. Vulcanizable
1. Diene rubbers
2. Nondiene rubbers
B. Nonvulcanizable and other elastomers

Class II. Hard plastics
Class III. Reinforcing resins
Class IV. Paint vehicles

Rubbers are further classified and coded from the chemical composition of the polymer chain in the following manner:

M Rubbers having a saturated chain of the polymethylene type
N Rubbers having nitrogen in the polymer chain, but not oxygen or phosphorus
O Rubbers having oxygen in the polymer chain
R Rubbers having an unsaturated carbon chain; e.g., natural rubber and synthetic rubbers derived at least partly from diolefins
Q Rubbers having silicone and oxygen in the polymer chain
T Rubbers having sulfur in the polymer chain
U Rubbers having carbon, oxygen, and nitrogen in the polymer chain
Z Rubbers having phosphorus and nitrogen in the polymer chain

The R class shall be defined by inserting the name of the monomer or monomers from which it was prepared before the word "rubber" (except for natural rubber). The letter immediately preceding the letter R shall signify the diolefin from which the rubber was prepared. Any letter or letters preceding this diolefin letter signify the comonomer or comonomers.

ABR	Acrylate-butadiene	NCR	Nitrile-chloroprene
BIIR	Bromoisobutene-isoprene	NIR	Nitrile-isoprene
BR	Butadiene	NR	Natural rubber
CIIR	Chloroisobutene-isoprene	PBR	Vinyl pyridine-butadiene
CR	Chloroprene	PSBR	Vinyl pyridine-styrene-butadiene
IIR	Isobutene-isoprene	SBR	Styrene-butadiene
IR	Isoprene, synthetic	SCR	Styrene-chloroprene
NBR	Nitrile-butadiene	SIR	Styrene-isoprene

SOURCE: *ASTM Standards*, Rubber and Rubber Products D1418-81 (Reprinted by permission of the ASTM from copyrighted material.)

Styrene is a monomer for rubber but is mainly used in the production of polystyrene plastics.[3] In 1981 the total styrene production in the United States was 3.04×10^6 t and it sold at 66 cents per kilogram: 1.58×10^6 t were consumed in producing polystyrene and 3×10^5 t in producing SBR copolymer. ABS resins used 9 percent of total production, polyester resins,

[3]Key Chemicals, *Chem. Eng. News* 60 (25) 17 (1982).

Table 36.5 Synthetic Elastomer Consumption (in thousands of metric tons)

	1979	1980	1981	1982*
SBR	1320	1010	996	1020
Butadiene	410	335	350	375
Ethylene-propylene	155	118	138	155
Butyl	141	128	130	132
Neoprene	122	105	98	105
Nitrile	76	63	68	75
Polyisoprene	74	63	50	55

*Estimated.

SOURCE: *Chem. Eng. News* 60 (10) 19 (1982)

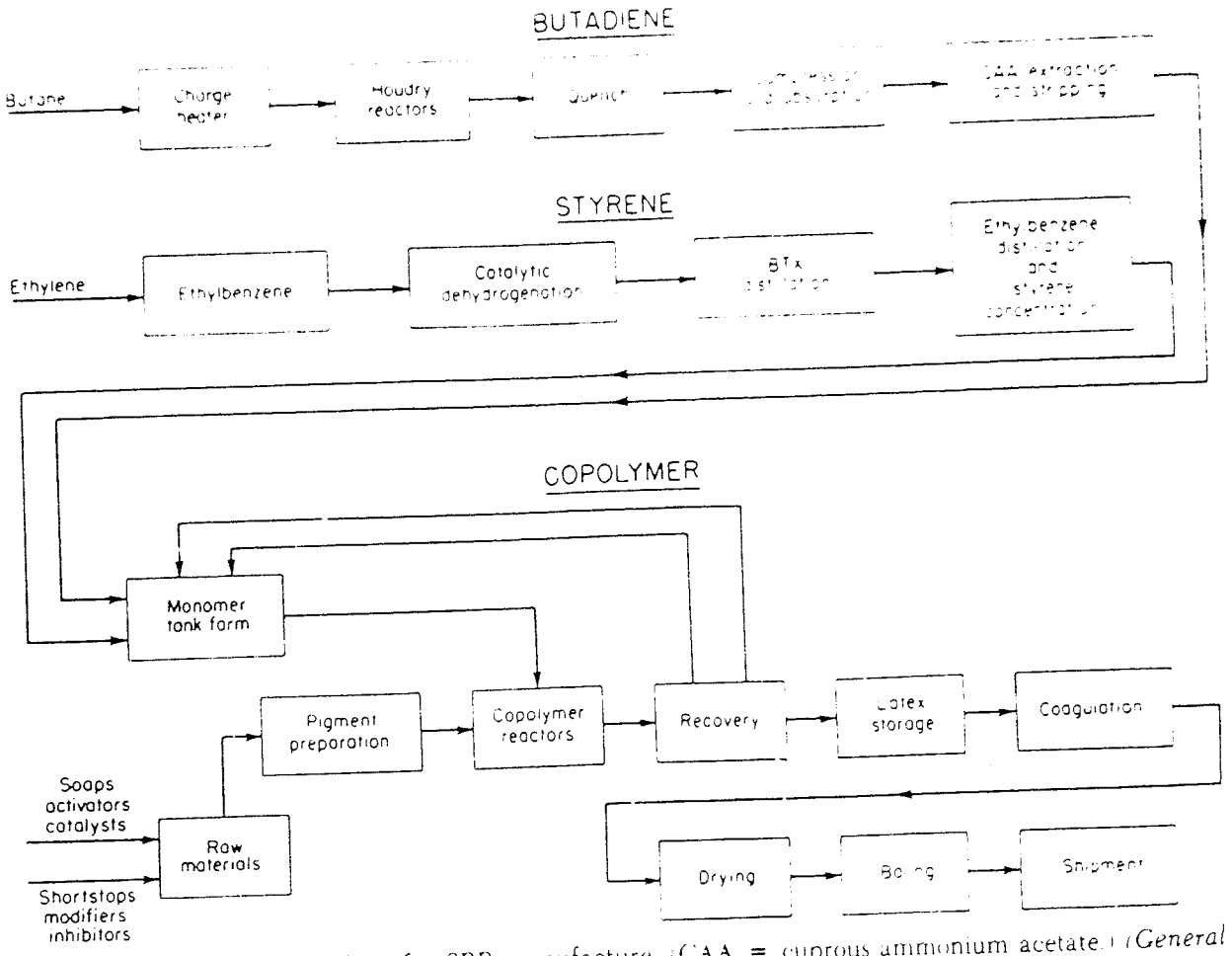


Fig. 36.1. Simplified flowchart for SBR manufacture (CAA = cuprous ammonium acetate.) (*General Tire and Rubber Co.*)

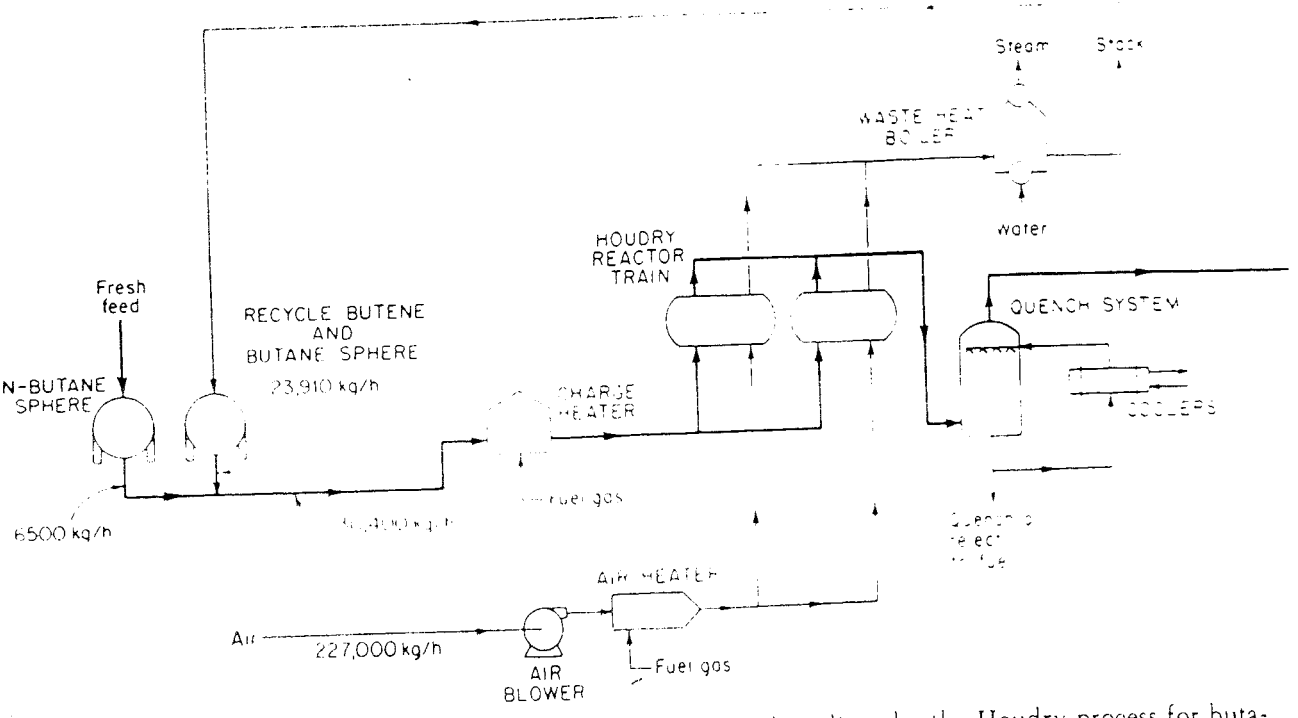


Fig. 36.2. Flowchart for the production of 29,000 t/day of butadiene by the Houdry process for butadiene by dehydrogenation of *n*-butane. The same process can also be used for manufacturing isoprene from isopentane. (*Catalytic Construction Co.*)

6 percent, styrene-acrylonitrile resins, 1 percent, and other uses 19 percent. The predominant route to the production[4] of styrene is via ethylbenzene, which is made by alkylating benzene with ethylene and subsequently dehydrogenating to styrene over an aluminum chloride, solid phosphoric acid, or silica-alumina catalyst (Figs. 36.1 and 36.3):

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5CH{=}CH_2 + H_2$$

Acrylonitrile[5] is principally made by the Sohio process that treats propylene with air and ammonia in a fluid-bed catalytic reactor.

$$CH_3CH{=}CH_2 + NH_3 + \text{air} \rightarrow CH_2{=}CHCN$$

The effluent is scrubbed in a countercurrent absorber, and the acrylonitrile is purified by fractionation. The yield is about 0.9 kg per kilogram of propylene fed.

Chloroprene, the monomer from which neoprene is produced, is manufactured from acetylene and hydrogen chloride. Acetylene is dimerized to monovinylacetylene, which is then reacted with hydrogen chloride to form chloroprene.

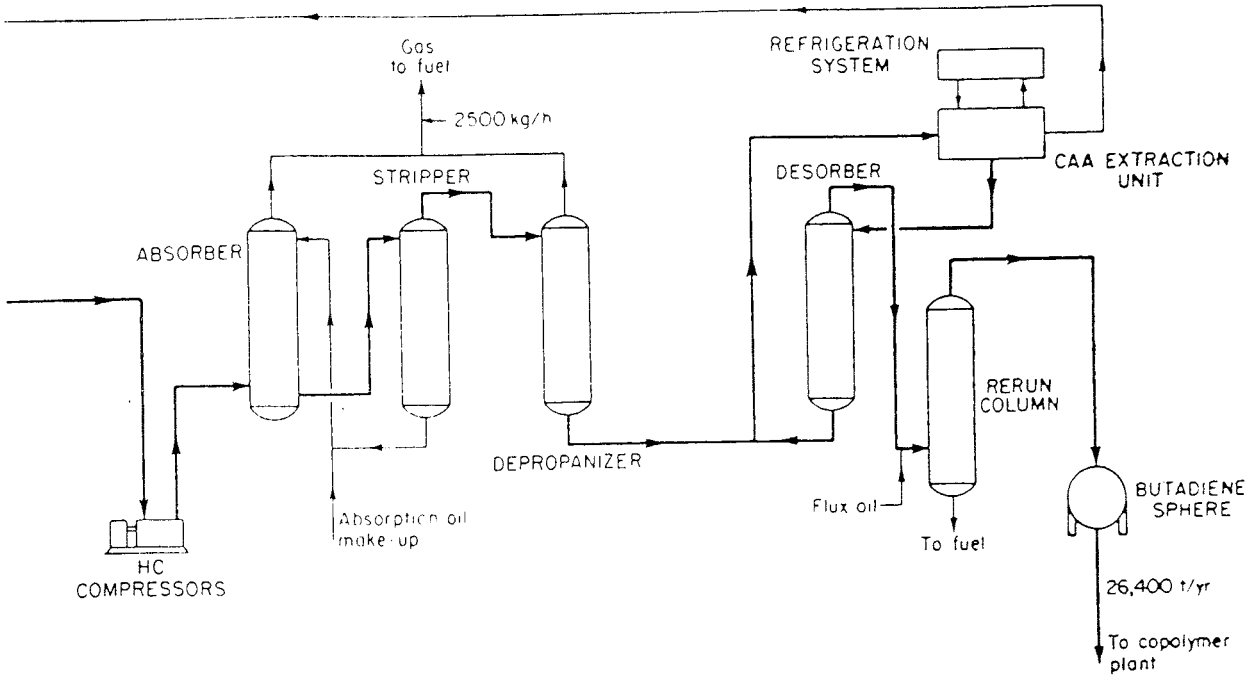
$$2CH{\equiv}CH \xrightarrow[18\text{-}24^\circ C\ 35\ kPag]{aq.Cu_2Cl_2\cdot NH_4Cl} \underset{\text{Vinyl acetylene}}{CH_2{=}CH{-}C{\equiv}CH} \xrightarrow{HCl} \underset{\text{Chloroprene}}{CH_2{=}CCl\cdot CH{=}CH_2}$$

Contact time is 10 to 15 s, conversion is 20 percent per pass, and yield is 60 to 65 percent.

Isobutylene is recovered from refinery light-end operations by distillation. It is the monomer for butyl rubber. See Table 36.3.

[4]Styrene flowcharts: *Hydrocarbon Process* 60 (11) 227 (1981).

[5]*Hydrocarbon Process*. 60 (11) 125 (1981).



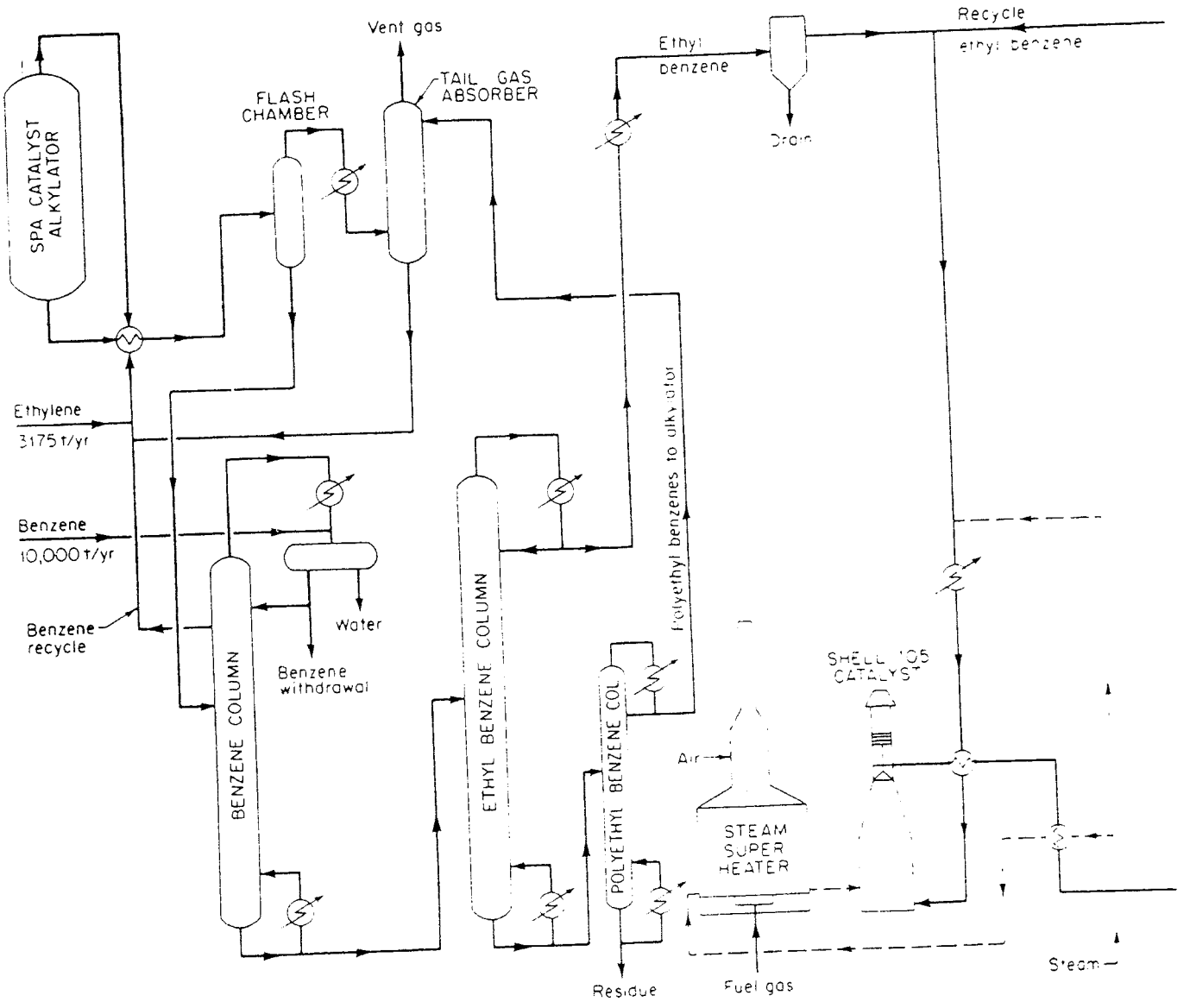


Fig. 36.3. Styrene, from ethyl benzene, 9000 t. (*Petrobras*)

Isoprene may be produced by the dehydrogenation of isopentane in the same plant as that shown in the butadiene flowchart in Fig. 36.2. However, the presence of 1,3-pentadiene (for which there is very little market) requires an expensive purification step. The Goodyear S-D method produces isoprene from propylene (reactions A). Production costs for this process are potentially quite low, and the raw material is cheap and plentiful.[6] Isoprene can be produced from isobutylene and methanol (reactions B), and the product is of exceptional purity when made by this method. This process has been developed by the Institut Francais du Petrole. The production of isoprene by reactions C was developed by the Italians (SNAM).

Reactions A

$CH_3-CH=CH_2$
Propylene

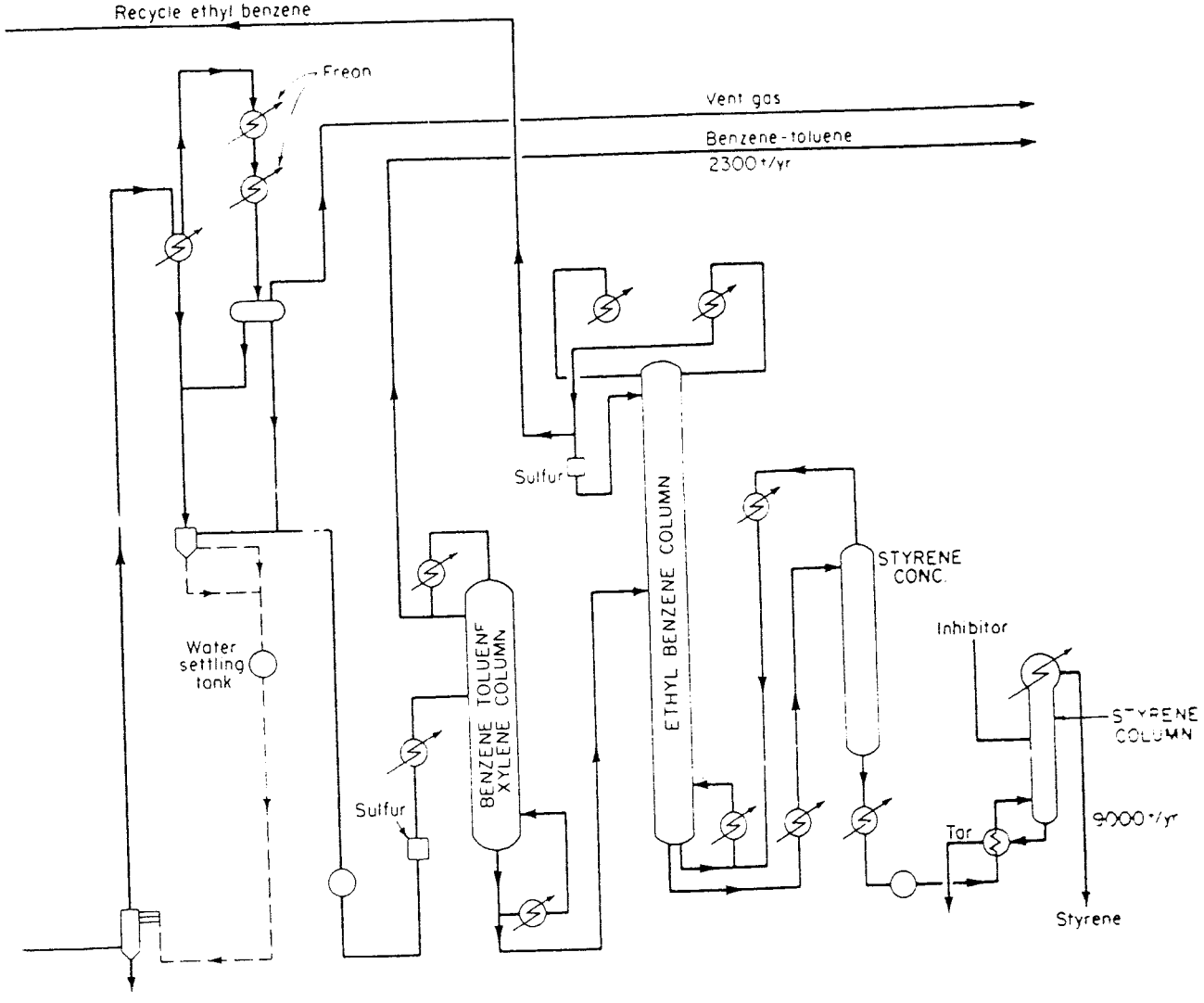
dimerization

Reaction B

Reaction C

$HC{\equiv}CH + CH_3-C{\equiv}CH$

[6]Better Route to Isoprene, *Hydrocarbon Process* 53 (7) 121 (1974); Saltman, *The Stereo*



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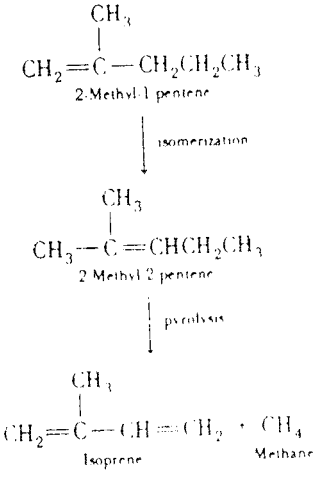
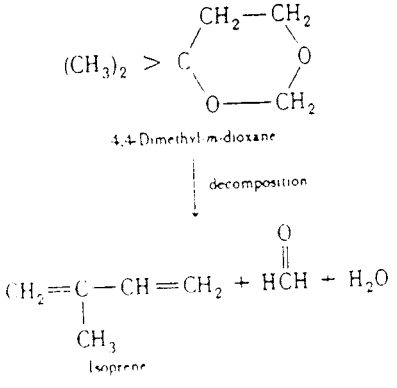
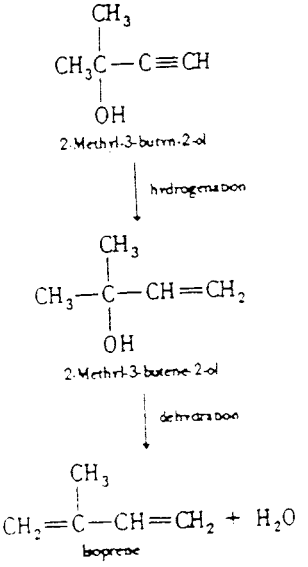
Reactions A



Reactions B



Reactions C



Ethylene and propylene are readily available from refinery light-end cuts or may be produced by the steam cracking of propane or heavier fractions (Chap. 37). The potential low cost of these materials as monomers for rubber and the very favorable results obtained, indicate a considerable future for rubbers produced from these petrochemicals.

Synthetic-Rubber Polymerization

The various methods of production of synthetic rubbers have much in common. The monomers are not particularly difficult to handle at reasonable pressures, and suitable inhibitors have been developed to impart storage stability. Flowcharts in the conventional simplified equipment form for the widely used SBR (Figs. 36.1, 36.4, and 36.5,) are typical, and several rubbers can be made interchangeably in such a plant. Dissipation of the heat of polymerization is frequently the controlling consideration. Adjustment of reaction rate to distribute the heat generation over a reasonable period of time, the use of refrigeration such as may be provided by ammonia coils within the reactors, and operation in dilute media such as emulsions or solutions are necessary for the adequate control of polymerization reactions (Fig 36.5).

Control of molecular weight[7] and of molecular configuration have become the predomi-

[7]MWD, or molecular weight distribution, is needed to control costs and quality

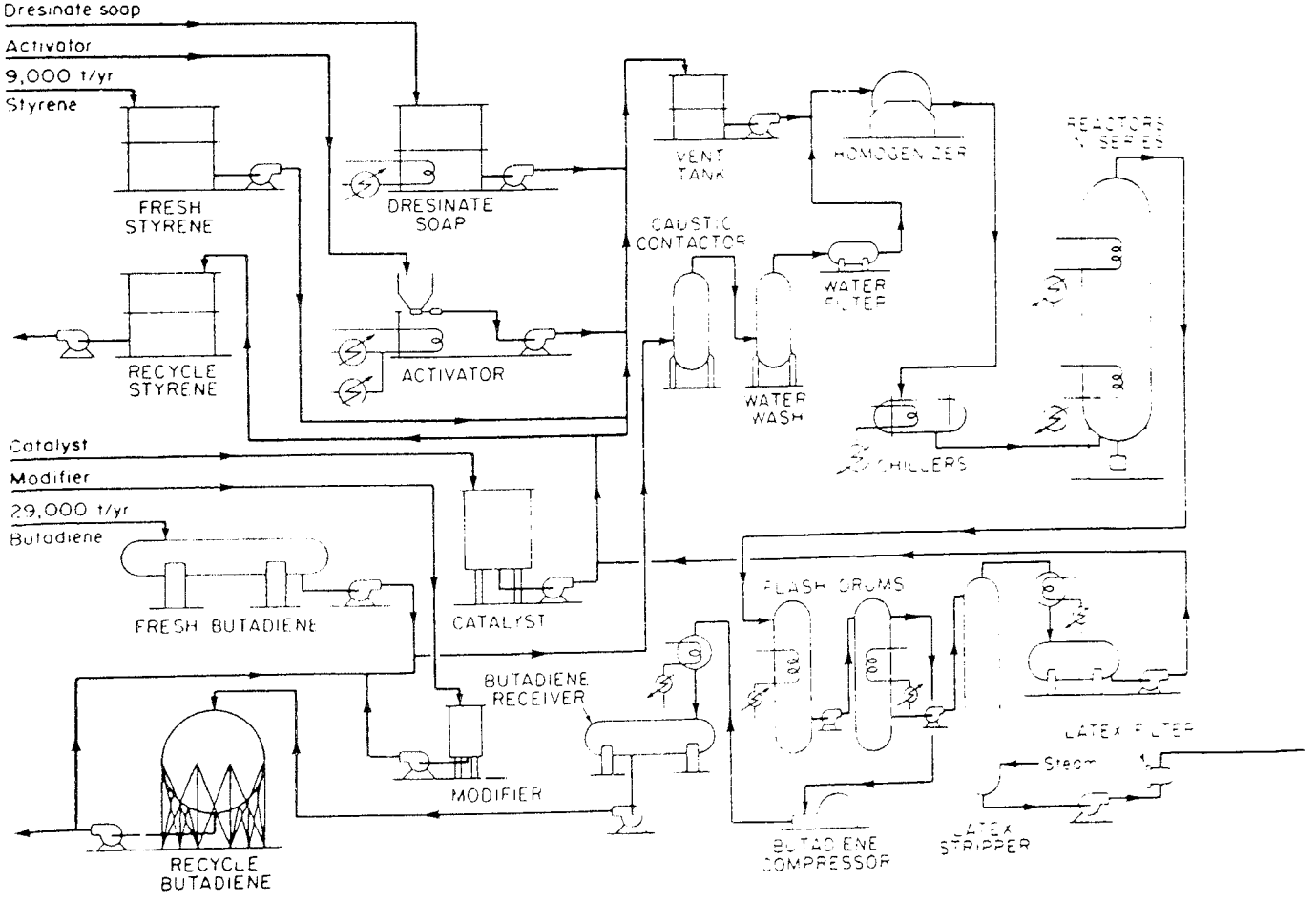
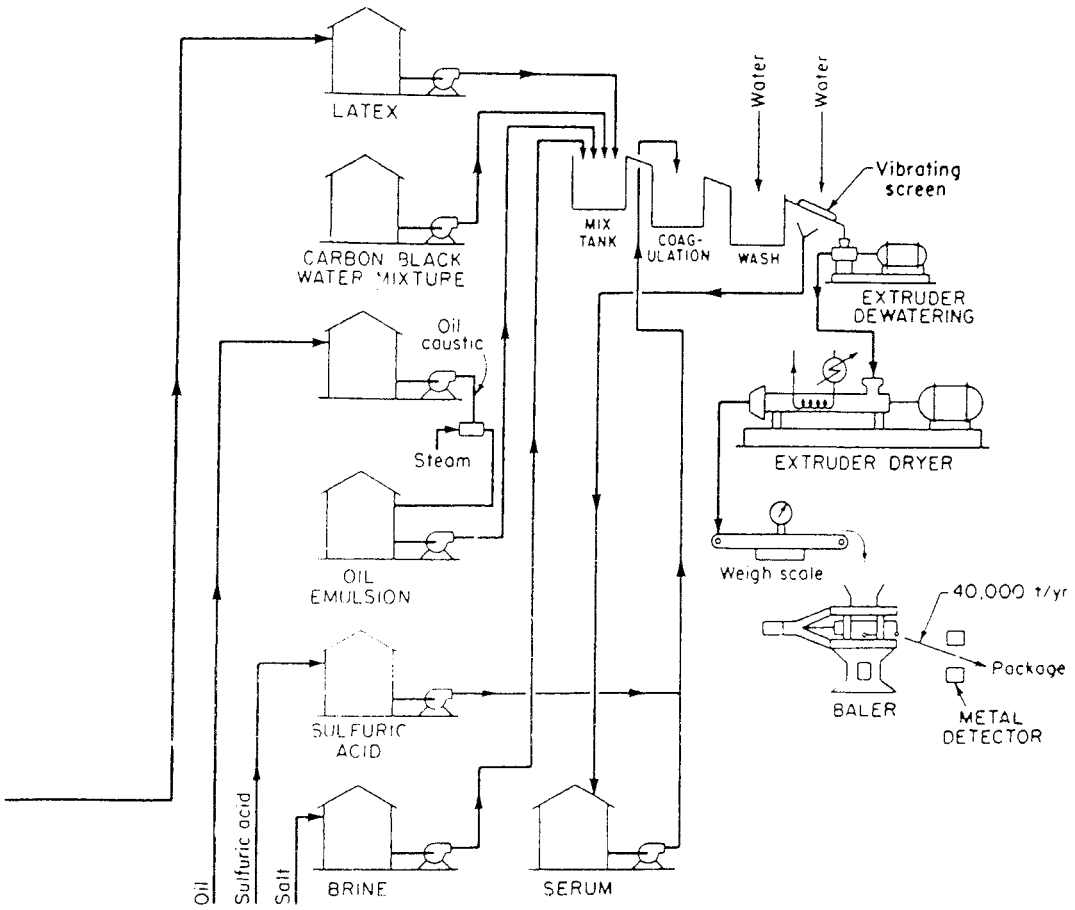


Fig. 36.4. Flowchart for SBR (and other copolymers).

nant quality considerations. See Stereospecific Copolymers. The ability to control molecular weight has led to the development of *oil-extended rubbers* (Fig. 36.4), which have had far-reaching effects on the industry. In late 1950, the General Tire & Rubber Co. applied for a patent and disclosed its process for the addition of petroleum oils to high-molecular-weight rubber. Not only does the oil render the extremely tough, high-molecular-weight rubber processible, but it allows much of the quality inherent in the tougher material to be retained and actually results in improvements in quality. Amounts of oil up to 50 parts per 100 parts rubber have become commonplace, and approximately 70 percent of the SBR produced in the United States is oil-extended, finding its principal use in tire-tread rubber. First successfully applied to SBR, the process has assumed great importance as ways to add oils to the newer stereoregular polymers have been discovered.

MONOMER RECOVERY. The rubber quality and rate of reaction both fall off as polymerization proceeds, and it is customary to stop the reaction short of complete conversion to rubber. Recovery of the unreacted monomers and purification is an essential step in economical synthetic-rubber production (Fig. 36.4). Methods of recovery by steam stripping from aqueous latices or by distillation from solvent systems are employed. In some cases, recovery of the monomer can be accomplished during the drying step in a devolatilizing extruder dryer as pictured in Fig. 36.6. Water or solvent is removed by a combination of mechanical squeezing and by passage through a vacuum section. The space, maintenance, and labor requirements of such dryers are sufficiently less than for the conventional multipass apron dryer, so that this unit has been installed in several new rubber plants.



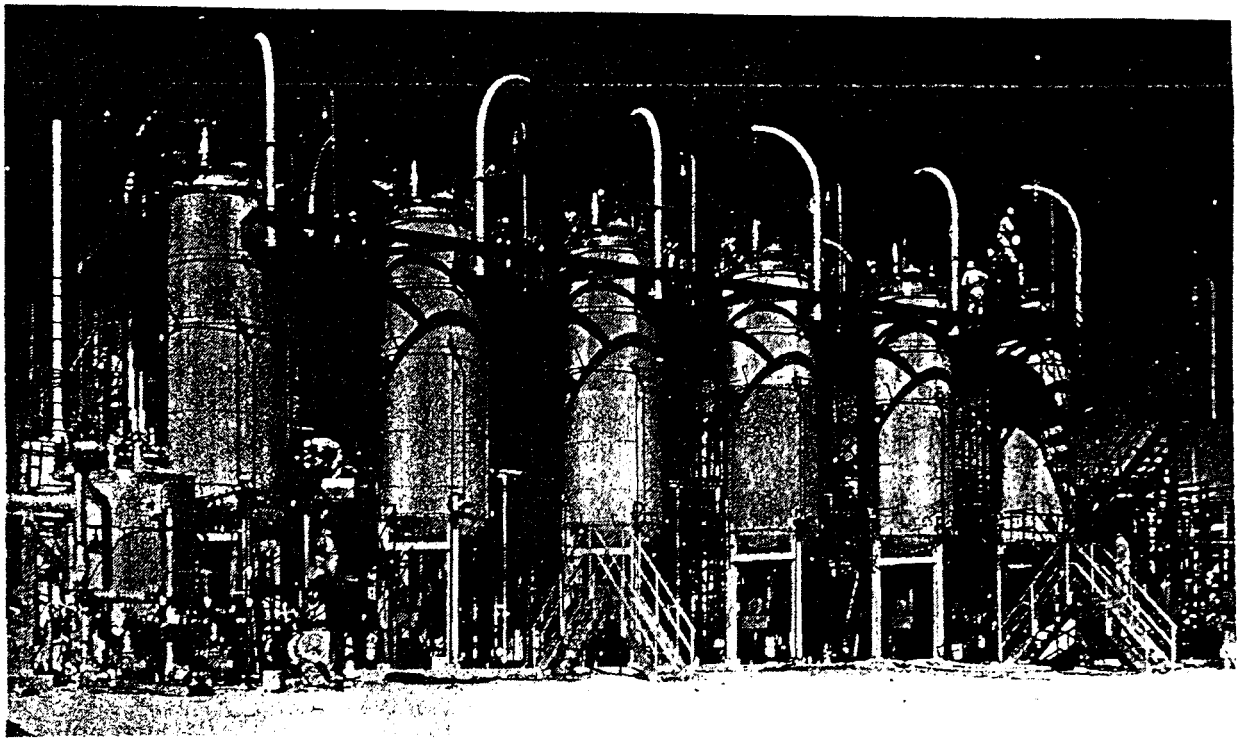


Fig. 36.5. Synthetic rubber reactors operated in series for a continuous reaction to produce SBR. (*General Tire and Rubber Co.*)

COAGULATION AND DRYING. The finishing process usually consists of precipitating the rubber from the latex emulsion or from the solvent solution in crumb form; it is then dried and compressed into a bale (Fig. 36.6). Ordinary latices may be easily coagulated by the addition of sodium chloride and dilute sulfuric acid, alum, or virtually any combination of electrolyte and dilute acid. The rubbers which result from solution polymerization can be precipitated into crumb form by adding the solution to a tank of hot water under violent agitation, with or without the addition of wetting agents, to control crumb size and prevent reagglomeration. The coagulated crumb is separated from the serum and washed on vibrating screens or rotating filters and dried at appropriate temperatures. Rubber is a difficult material to dry, and care must be taken not to overheat it or otherwise cause its deterioration. Drying times in conventional hot-air apron dryers may be as long as several hours.

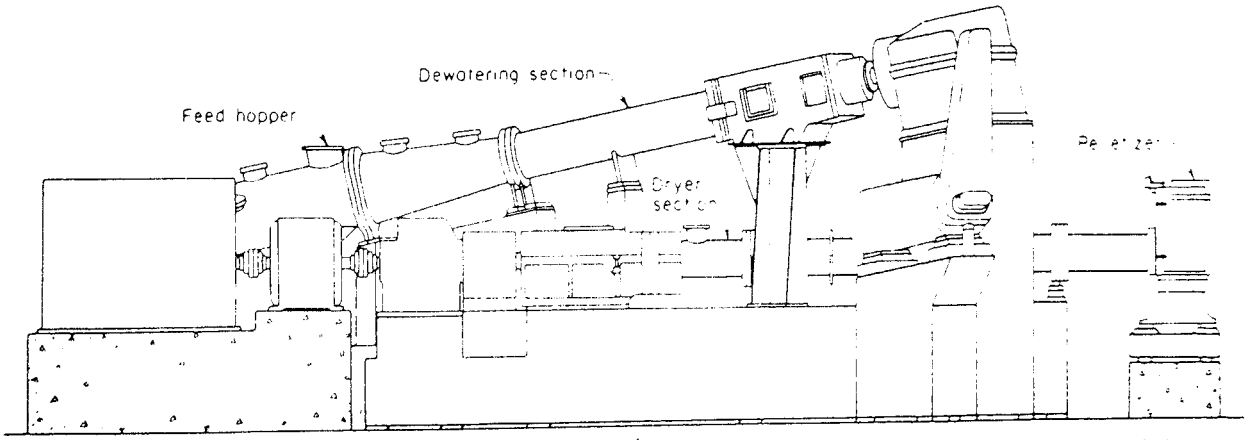


Fig. 36.6. Dual worm rubber dryer or dewaterer. This accepts a slurry feed of 50% or more solids containing 1 to 2% hydrocarbons and devolatilizes and dries to less than 0.3% volatiles. Throughput rates are up to 2300 kg/h with continuous feed, using 485 kJ and 315 MJ/h jacket heating. Typical elastomers handled by this equipment are butyl rubber, *cis*-polybutadiene, and *cis*-polyisoprene. (*Welding Engineers.*)

PACKAGING. Synthetic-rubber packaging is important, since problems involving adherence to the package and contamination resulting from inadequate protection are sometimes difficult to cope with because of the tendency of some of the rubber to flow and fail to retain its shape. Most rubber is now wrapped in polyethylene film as a 34-kg bale of reasonably standard dimensions. In most cases, it is possible to throw bale and polyethylene wrapping into the rubber mill or internal mixer, since the polyethylene melts at a temperature lower than the usual rubber-processing temperatures.[8]

BUTADIENE-STYRENE COPOLYMERS.[9] The copolymers of styrene and butadiene that contain over 50% butadiene are known as SBR. The usual monomer ratio is 70 to 75 parts of butadiene to 30 to 25 parts of styrene. As the styrene content is increased above 50%, the product becomes increasingly plastic and is used in latex paint. A typical recipe for SBR is given in Table 36.6. The polymerization is carried out in an emulsion at about 5°C and requires 8 to 12 h. A series of reactors, such as those shown in Fig. 36.5, are often used. The heat of polymerization is approximately 1280 kJ per kilogram of rubber produced and is removed by internal ammonia coils. The molecular weight of the polymer is regulated by the use of a modifier, such as a tertiary C_{12} mercaptan, which regulates chain growth. The reaction is terminated at 60 to 75 percent of completion because higher conversion gives polymers with inferior properties that are due to cross-linking and branching. Sodium nitrite and sodium dimethyldithiocarbamate are added to terminate the reaction. The unreacted butadiene is flashed off, and the styrene is recovered by steam distillation.

The emulsion, in effect a latex,[10] is accumulated in holding tanks and blended to the proper specifications for the grade of rubber required. It is coagulated and extensively washed and dewatered prior to the drying operation. Much of the SBR is extended with oil before it is vulcanized. The softening effects of the oil are counterbalanced by the addition of carbon black. Much of the SBR sold is in the form of master batches, in which the oil and carbon have already been added.

Emulsion polymerization produces a random distribution of the polymer units. A typical SBR produced by emulsion polymerization contains 23% styrene units, and the butadiene units (77% of the total) have the configuration of 65% *trans*-1,4, 18% *cis*-1,4, and 17% vinyl-1,2.

Styrene-butadiene copolymers may also be produced by solution polymerization. Solution

[8]Rubber Handling: Crumb to Bale, *Hydrocarbon Process.* 53 (3) 79 (1974).

[9]ECT, 3d ed., vol. 8, 1979, p. 608; Saltman, op.cit.

[10]Suspension of rubber particles 40 to 200 nm in size

Table 36.6 Typical Recipe for Cold Emulsion SBR

	Parts by Weight	Function
Butadiene	72	Monomer
Styrene	28	Monomer
d-Isopropyl benzene hydroperoxide	0.08	Catalyst
Ferrous sulfate	0.14	Activator
tert-Dodecyl mercaptan	0.2	Modifier
Potassium pyrophosphate	0.18	Buffer
Rosin acid soap	4.0	Emulsifier
Water	180	

SOURCE: Allen, *Natural Rubber and the Synthetics*, Wiley, New York, 1972.

polymerization allows the operator to have some control over the stereostructure of the resulting polymer and thus, over the physical properties. A typical solution SB polymer contains 35 to 40% *cis*-1,4, 50 to 55% percent *trans*-1,4, and 10% vinyl-1,2-butadiene units. The styrene units are randomly distributed along the chain. This polymer has better abrasion and fatigue resistance, higher resilience, and lower heat build-up than emulsion polymerized SBR.

Block polymers of styrene and butadiene may also be produced by special polymerization conditions (Chap. 34). These polymers are thermoplastic and do not require vulcanization to be useful.

SBR rubber does not crystallize when stretched, as natural rubber does, and thus is very weak unless reinforced with carbon black or other materials. It is, even then, less strong than natural rubber. Its vulcanization properties are good and the ageing characteristics are satisfactory. Over 70 percent of the SBR produced is used for tire and tread rubber, 15 percent for mechanical goods, and about 10 percent is sold as latex

NITRILE RUBBERS (NBR). Copolymers of butadiene and acrylonitrile are made similarly to SBR by emulsion polymerization. The acrylonitrile content of the copolymer may be varied from 20 to 50% depending upon the properties desired. Resistance to hydrocarbons, solvents, abrasion, and gas permeation increases with increasing nitrile content. Decreasing the amount of nitrile present increases the low-temperature properties and resilience. NBRs are resistant to oils, solvents, water, salts, aliphatic compounds, soaps, and most foods. They are serviceable for continuous use up to 120°C in air and to 150°C immersed in oil.

NEOPRENE. Polychloroprene was developed by DuPont and sold commercially in 1932, first under the name DuPrene, but later as Neoprene. It is prepared by emulsion polymerization of purified chloroprene at about 38°C in the presence of sulfur. It is resistant to oxidation, oil, and heat, is flame resistant, and finds specialty uses, especially in automotive parts, adhesives, sealants, and coatings. It is more expensive than natural rubber and thus is only used where its special properties are needed.

THIOKOL. Thiokol, a polysulfide type of rubber, was first developed in this country in the early 1920s and was the first commercial synthetic rubber produced in the United States. Thiokols are prepared by the condensation polymerization of an alkaline polysulfide with a suitable organic dihalide.

$$n\underset{\text{Dichloroethyl formal}}{ClCH_2CH_2OCH_2OCH_2CH_2Cl} + n\underset{\text{Sodium polysulfide}}{Na_2S_2} \longrightarrow \underset{\text{Thiokol}}{(-CH_2CH_2OCH_2OCH_2CH_2SS-)_n} + 2nNaCl$$

Various sodium polysulfides may be reacted with organic dihalides to give specialty rubbers of somewhat different properties, and are particularly useful for linings for petroleum tanks, for building and caulking putties, cements, and sealants, and lately for rocket-fuel binders, ablative coatings, and other items requiring ease of application and good weathering resistance.

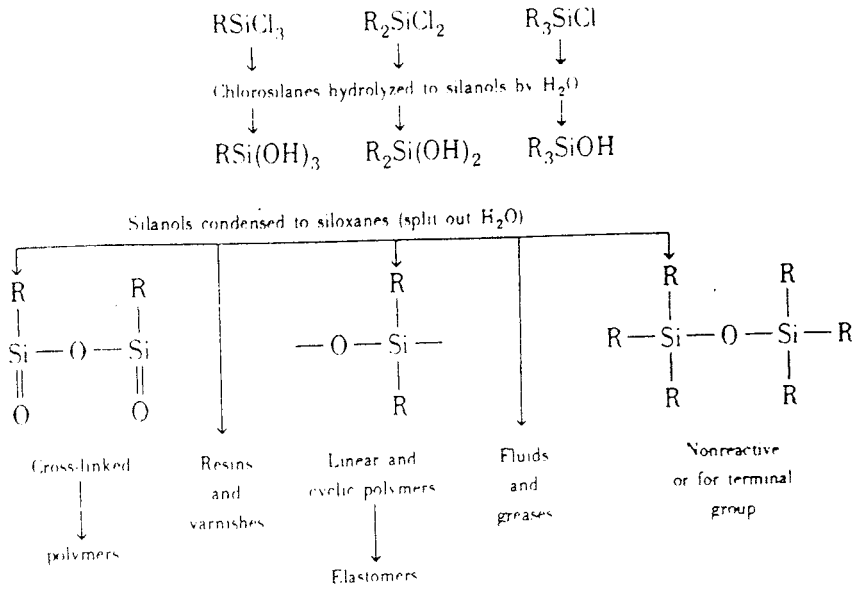
SILICONE RUBBERS. Silicone rubbers are mixed inorganic-organic polymers produced by the polymerization of various silanes and siloxanes. Although expensive, their outstanding resistance to heat makes them uniquely useful for high-temperature applications. The chain is based on alternate atoms of silicon and oxygen, with no carbon. Silicones and their derivatives are remarkable in the variety and unusualness of their properties, such as solubility in

organic solvents, insolubility in water and alcohols, heat stability (−62 to 200°C), chemical inertness, high dielectric properties, relatively low flammability, low viscosity at high resin content, low viscosity change with temperature, and nontoxicity. Because of these properties, silicones are useful in fluids for hydraulics and heat transfer, lubricants and greases, sealing compounds for electrical applications, resins for lamination and for high-temperature-resistant varnishes and enamels, silicone rubber, water repellents, and waxes and polishes. The largest consumption of silicone rubbers is by the aerospace industry which uses them for deicing equipment, gaskets, ablation shields, and similar temperature-demanding applications.

Silicones[11] are made either by the Grignard reaction, or more economically, by alkylating with an organic halide, usually CH_3Cl (or C_6H_5Cl or mixtures thereof), and a silicon-copper alloy, according to the following reaction:

$$Si(10\%\ Cu) + nCH_3Cl \xrightarrow[48\ h]{200°C,\ 100\text{-}200\ kPa} (CH_3)_nSiCl_{(4-n)}$$

The principal products are the chlorosilanes: $(CH_3)_2SiCl_2$, $(CH_3)_3SiCl$, CH_3SiCl_3. The chain length of the polymers is varied by the percentage of R_3SiCl, which provides the end groups. Lower polymers are oils, higher polymers are solids. The silicon or copper may absorb any excess chlorine. Further reactions to silanols, siloxanes, and polymers may be expressed:



The production of silicone products for elastomers in 1978 was 27×10^6 kg worth about $210 million.

BUTYL RUBBER. The copolymer of isobutylene with about 2% isoprene is known as butyl rubber. The isoprene imparts sufficient unsaturation to the molecule to permit curing or vulcanization. The polymerization is carried out in a slurry of the monomers in methyl chloride using an aluminum chloride catalyst at −100 to −90°C. The reaction is very fast and produces 2000+ monomer linkages.[12] The rubber is precipitated by adding water and separates

[11]Rochow, *An Introduction to the Chemistry of the Silicones*, 2d ed., Wiley, New York, 1936; *General Electric Materials Technology*, spring 1980; Schiefer and Pope, Use of Silicones in Process Plants, *Chem. Eng.* 89 (3) 123 (1982).

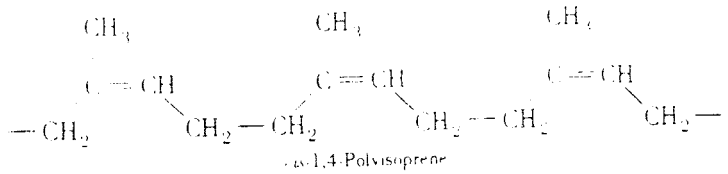
[12]ECT, 3d ed., vol. 8, 1979, p. 470.

as a crumb. Butyl rubber has extremely low permeability to gases and thus its major use is in inner tubes and in linings for tubeless tires. Butyl rubber is also inert to oxidation and is useful for weatherstripping. A variant, halogenated butyl rubber, has even better resistance to ageing, is more compatible with other rubbers, and is used in tubeless tires.

URETHANE RUBBER. The reaction products of certain organic diisocyanates and polyglycols are rubbery products known as polyurethanes.[13] These compounds are specialty rubbers with outstanding properties as they possess high abrasion resistance and are useful at high temperatures and with high concentrations of solvents and oxygen or ozone. A major use for this type of rubber is in the production of flexible foam and elastic fibers, which result when a diisocyanate is mixed with a polyester containing both free hydroxyl and carboxyl groups. The reaction is extremely rapid, with the evolution of gas which serves to expand the mass yielding foams, either hard or soft, depending on the reactants and the conditions employed. These materials have found increasing use in upholstery, mattresses, insulation, vibration damping, and other fields of application formerly restricted to foam rubber. The tensile strength and abrasion resistance of polyurethanes are extraordinary in comparison with those of hydrocarbon elastomers. Both rigid and flexible foams have encountered difficulties in some applications because of flammability. The appearance of spandex (Chap. 35) polyurethane elastic thread has revolutionized the support-garment field because of the high holding power of fine-denier thread.

HYPALON. A rubber called Hypalon results from the free-radical catalyzed reaction of chlorine and SO_2 with polyethylene, transforming the thermoplastic polyethylene into a vulcanizable elastomer. Hypalon is extremely resistant to ozone attack, weathering, and heat and has excellent chemical resistance.

STEREOSPECIFIC RUBBER- POLYISOPRENE AND POLYBUTADIENE. The discovery that catalysts of the Ziegler-Natta (alkyl lithium) type would catalyze polymerization of isoprene or butadiene to produce mainly the cis structure made it possible to nearly duplicate natural rubber synthetically. Polyisoprene (IR) is



cis-1,4-Polyisoprene

and is essentially identical with natural rubber and has the advantages of being of better color, more uniform in quality, lower odor, faster processing breakdown and mixing, better extrusion and calendering, excellent mold flow, and a controlled molecular weight. In contrast, natural rubber has higher tear strength, tack, and tensile strength. IR is produced commercially and is used along with, or substituted for, natural rubber (Fig. 36.7).

The lower cost and availability of butadiene, relative to isoprene, have caused polybutadiene to be produced in much greater quantities than polyisoprene (Table 36.5). It is the third most used rubber after SBR and NR. Stereoregular polybutadiene (BR) can be produced in

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[13]Frisch and Reegan, *Advances in Urethane Science and Technology*, Technomic, Westport, Conn., vols. 1–7, 1971–1979; *Urethane Chemistry and Applications*, ACS, Columbus, Ohio, 1981.

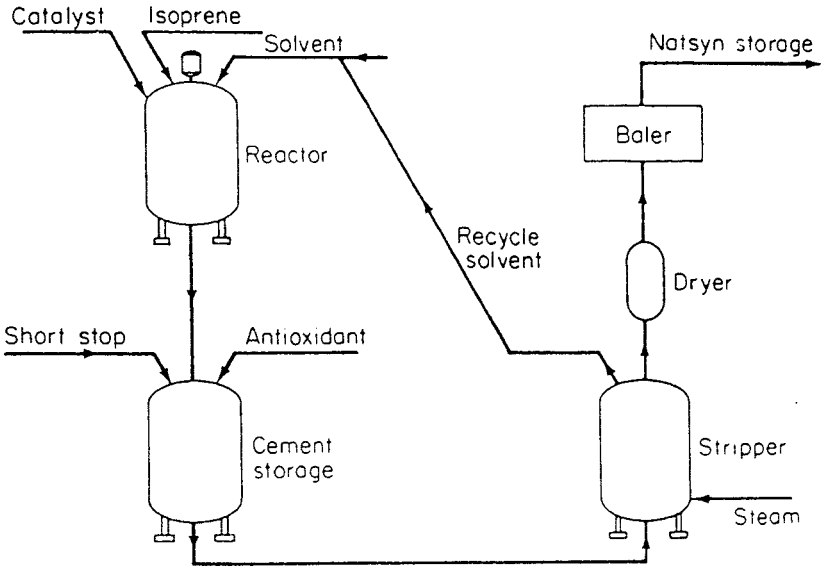

Fig. 36.7. Natsyn process for synthetic natural rubber production (synthetic polyisoprene) *(Goodyear Tire and Rubber Co.)*

modified SBR plants. The catalyst used determines the configuration of the polymer.[14] If a Ziegler-type catalyst (organic aluminum compound plus a titanium, cobalt, or nickel compound) is used, polymers of up to 90% cis form can be produced. On the other hand, anionic catalysts, such as butyl lithium, produce polymers containing about equal quantities of cis and trans forms, while vanadium chloride or rhenium and nickel complexes yield almost pure trans form. The other type of polymer obtained from 1,4-butadiene is the vinyl- or 1,2-polybutadiene. This can be produced in good yields using a halogen-free vanadium compound with an aluminum alkyl as a cocatalyst.

High *cis*-1,4-polybutadienes are soft, easily solubilized, and have low hysteresis and good abrasion resistance. High *trans*-1,4-polymers are rigid, crystalline, and have poor solubility characteristics. These can be used to replace gutta-percha for golf ball covers. The usual polybutadiene rubbers produced are alkyl lithium catalyzed and contain medium amounts of the cis isomer. Polybutadiene is used to extend and partially replace both NR and SBR in tires. The usual tire contains 25% polybutadiene, and this use accounts for 85 percent of the butadiene produced.

ETHYLENE-PROPYLENE POLYMERS AND TERPOLYMERS.[15] Copolymers of ethylene and propylene (EPM), made by solution polymerization using a Ziegler-type catalyst, are elastomers but do not contain any double bonds. Thus, they cannot be vulcanized but neither are they attacked by oxygen and ozone. The reactivities of ethylene and propylene are quite different, and thus the monomer composition differs from that of the copolymer formed. This offers difficulties in preparing a uniform polymer and requires that the monomer composition be kept constant during the course of the polymerization. EPR may be vulcanized by heating with a peroxide which cross-links the chains by joining carbon atoms directly to each other, instead of through a sulfur linkage as in the usual process. These rubbers may be used without vulcanization for many purposes.

[14]ECT, 3d ed., vol. 8, 1979, p. 546.

[15]Walker (ed.), *Handbook of Thermoplastic Elastomers*, Van Nostrand Reinhold, New York, 1979; Saltman, op. cit.; Allen, op. cit.

To promote easier vulcanization, terpolymers of ethylene-propylene and a diene (EPDM) have been prepared. The diene is used only in very small amounts and should contain one double bond that is capable of polymerizing with ethylene and propylene and one that can be used for vulcanization. It is also desirable that the second double bond not be in the main chain of the finished polymer. Conjugated double-bond compounds are not suitable. Compounds such as 1,4-hexadiene and dicyclopentadiene are commonly used.

EPDM polymers are exceptionally resistant to heat, oxygen, and ozone, and are widely used as roofing materials where they are replacing hot asphalt. Other uses are in wire and cable insulation where they are competing with neoprene.[16]

RUBBER COMPOUNDING

Pure rubber (natural or synthetic) is usually not suitable for use. The desirable properties of plasticity, elasticity, toughness, hardness or softness, abrasion resistance, impermeability, and the myriad combinations possible are achieved by the art of the rubber compounder.[17] A typical rubber compound is shown in Table 36.7. Rubber-processing chemicals production in 1980 was 132,000 t. Sales were 88,000 t and were valued at $296 million.[18]

These chemicals are divided into groups according to their uses (Table 36.8).

The *vulcanizing* agents are usually sulfur compounds which react with the polymer to produce a cross-linked material in which the linkages are $-C-S_x-C-$. The cross links may be mono-, di-, or polysulfidic. The type of linkage is determined by the concentrations of sulfur, accelerators, and retarders, and temperature. Most of the conditions to produce a given product are empirical, but some advances in knowledge are beginning to allow a scientific basis for vulcanizing conditions.

The *accelerators* reduce the time required for the vulcanization of rubber from several hours to a few minutes. In addition, less sulfur is needed and a more uniform product is obtained. The mechanism of accelerator action is not well understood, in spite of much research, but presumably involves the formation of an activated form of sulfur, which forms a "sulfur bridge" at reactive sites within the rubber molecule, linking the large molecules into

[16]EPDM Finds a Home as a Roofing Material, *Chem. Week* **128** (17) 13 (1981); Uniroyal Copolymer Challenges Neoprene, *Chem. Eng. News* **60** (35) 5 (1982).

[17]*Additives for Rubber and Plastic*, Chemical Marketing Research Association, 1977; Coran, The Art of Sulfur Vulcanization, *CHEMTECH* **13** (2) 106 (1983).

[18]*Synthetic Organic Chemicals, 1980, U.S. Production and Sales*, U.S. International Trade Commission, 1981.

Table 36.7 Typical Rubber Compound

Ingredient	Parts	Ingredient	Parts
Rubber	100.0	Loading or filling pigment	50.0
Sulfur	2.0	Reclaim, softeners, extenders, colors, blowing agents, antioxidants, antiozonants, odorants, etc.	As required
Zinc oxide	5.0		
Stearic acid	3.0		
Accelerator	1.5		

Table 36.8 Rubber-Processing Chemicals

Type of Agent	Chemical Compounds
Vulcanizing or curing	Sulfur, sulfur monochloride, selenium, tellurium, thiuram disulfide, polysulfide polymers, *p*-quinone dioxime
Accelerators	2-Mercaptobenzothiazole, benzothiozolyl disulfide, zinc diethyldithiocarbamate, tetramethyl mono- and disulfides, 1,3-diphenylguanidine
Accelerator activators	Zinc and magnesium oxides, stearic acid litharge, amines, amine soaps
Retarders	Salicylic and benzoic acids, phthalic anhydride
Antioxidants	*N*-Phenyl-2-naphthylamine, alkylated diphenylamine, acetone-diphenylamine condensate
Antiozonates	Derivatives of *p*-phenylene diamine
Fillers	Carbon black, clays, silica, zinc oxide, calcium carbonate
Softeners and extenders	Petroleum oils, pine tars and resins, coal-tar fractions
Blowing	Sodium or ammonium bicarbonate, diazoaminobenzene, dinitrosopentamethylenetetramine, fluorocarbons, azodicarbonamide nitrosoterephthalimide
Chemical plasticizers	2-Naphthalenethiol, bis(*o*-benzaminophenyl)disulfide, mixed xylene thiols
Peptizers	Aromatic mercaptans (thiophenols)

a tight network structure. Most accelerators contain nitrogen and sulfur. Two-thirds of all the accelerators made consist of mercaptobenzothiazole (MBT) and its derivatives. The commercial process for the manufacutre of MBT comprises reacting aniline, carbon bisulfide, and sulfur at a temperature of about 250°C and a pressure of at least 3.1 MPa. The crude product is dissolved in caustic, insoluble tars are removed, and the resulting solution is used for the manufacture of various derived accelerators, including refined MBT, benzothiazyl disulfide (MBTS), the zinc salt of MBT, and *N*-cyclohexybenzothiazole sulfanamide.

Age resistors, or antioxidants, protect rubber goods from attack by oxygen and ozone in the atmosphere. They are classified as antioxidants, antiozonants, or antiflex-cracking agents. They function by combining with, and thus interrupting, free-radical chain reactions and thus prevent further chain degradation. Commercial age resistors are generally either of the amine type or the phenolic type. Amines are strong protective agents and are widely used in tires and other dark-colored goods where discoloring or staining is not a problem. Examples of amine age resistors are alkylated diphenylamines, alkylated and arylated *p*-phenylenediamines, and complex reaction products of aromatic amines with aldehydes or ketones. In the case of light-colored goods, alkylated phenols and their derivatives are used to give moderate antioxidant protection with minimum discoloration.

Catalytic plasticizers, or *peptizers*, serve to reduce the viscosity of rubber to permit easier processing. When milled into the rubber, they cause chain scission, with a consequent lowering of the molecular weight. Peptizers are useful both in reclaiming vulcanized rubber and in softening high-molecular-weight crudes.

Large amounts of *inert filling materials* may be added to rubber. Some merely serve to harden or to dilute the mix. Others exert a profound influence called reinforcement, which is chemicophysical in nature. Clays, calcium carbonate, crushed coal, barytes—almost any finely divided solid—can be added to rubber, usually with a reduction in all tensile properties but with a desirable cost reduction, along with imparted hardness, retention of shape, color,

and other desirable properties. However, some finely divided amorphous materials, notably *carbon black* and *silica*, unexpectedly greatly increase the strength, resilience, abrasion resistance, and other desirable properties and are properly known as reinforcing agents.

Processibility is improved by the use of reclaimed rubber, waxes, oils, factices (vulcanized vegetable oils), and mineral rubbers (asphalts, pitches, and vulcanized unsaturated hydrocarbons) or by chemical attack on the molecule, as well as by work breakdown, heat, and mastication.

Sponge structure is obtained by adding sodium bicarbonate, ammonium carbonate and bicarbonate, urea, or organic gas-generating chemicals. *Hard rubber* may be made by greatly increasing the sulfur content and by the use of large amounts of filler.

RUBBER FABRICATION

As a plastic material, rubber may be spread, cemented, calendered, molded, extruded, caulked, puttied, or wrapped into virtually any shape; coated on cloth, plastic, or metal; and sandwiched or forced into cracks. Rubber is an extremely tough material. Heavy machinery is required, some of which is shown in the flowchart of Fig. 36.8 and in Figs. 36.9 and 36.10. The considerable heat generated during the mixing, mastication, grinding, and extruding must be dissipated and controlled. Some typical rubber-goods manufacture is briefly described.

CALENDERING, OR COATING. One of the earliest uses for rubber was for coating fabric to make it waterproof. Solutions or cements of rubber in solvents are easily spread on fabrics but, unless the ingredients necessary for cure and property control are included, the results may be quite unsatisfactory. Rubber compounds are applied to fabric by calendering, i.e., rolling the rubber compound into the fabric on multiroll calender machines. Tire cord is a special case in which cotton, rayon, nylon, or polyester cords are arranged in parallel and bound together by rubber on a calender.

MOLDING. Doughlike rubber compounds may be molded into virtually any shape, which is retained by curing the compound in the mold. A tennis ball is a good example. A very high grade and resilient rubber compound is molded in "muffin tins" shaped as halves of the ball. These are cemented together (with a pill of a gas-releasing chemical enclosed) and vulcanized to form the core of a ball, to which the fabric cover and proper nap fiber are cemented. It is a complicated structure for very rugged service.

EXTRUDING. Weatherstrip, hose, inner tubes, tire treads, gaskets, channels, and many other rubber articles are fashioned by extrusion of the plastic compound, which may be cured during this operation or later. The automobile tire serves as an example. Transportation is the major end use of rubber, and the tire its supreme product. Tire manufacture is depicted in Figs. 36.8 to 36.10. These illustrations show the many steps involved and make clear how the tire is shaped from wire, cord, fabric, and rubber into the doughnut shape which hugs the vehicle rim, retains air for months or years, resists the heat built up by service and the attack of air, ozone, oils, and chemicals, and provides tens of thousands of miles of travel over roads and highways of all types and all of a highly abrasive nature.

The tire is *built up as a cylinder* on a collapsible, round rotating drum. Layers of cords embedded in a proper compound are applied, one layer tying the beads together in one direc-

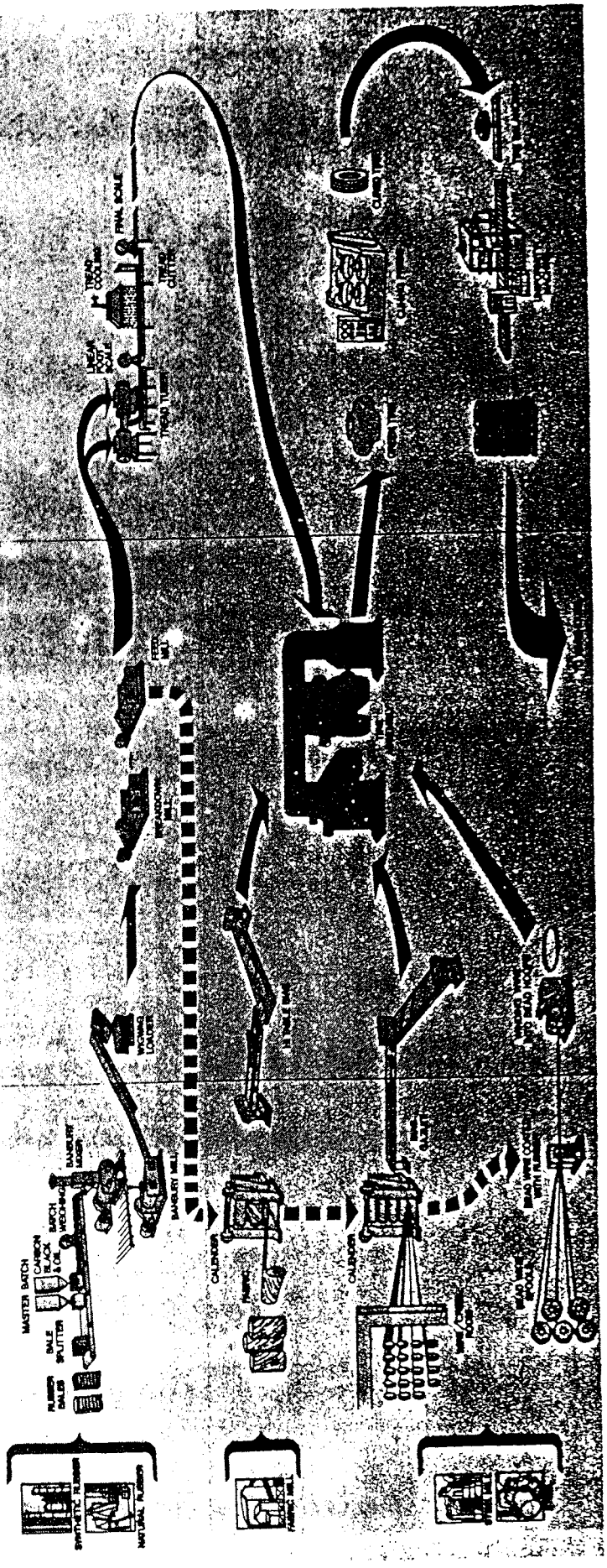

Fig. 36.8. Radial tire manufacturing process. *(General Tire and Rubber Co.)*

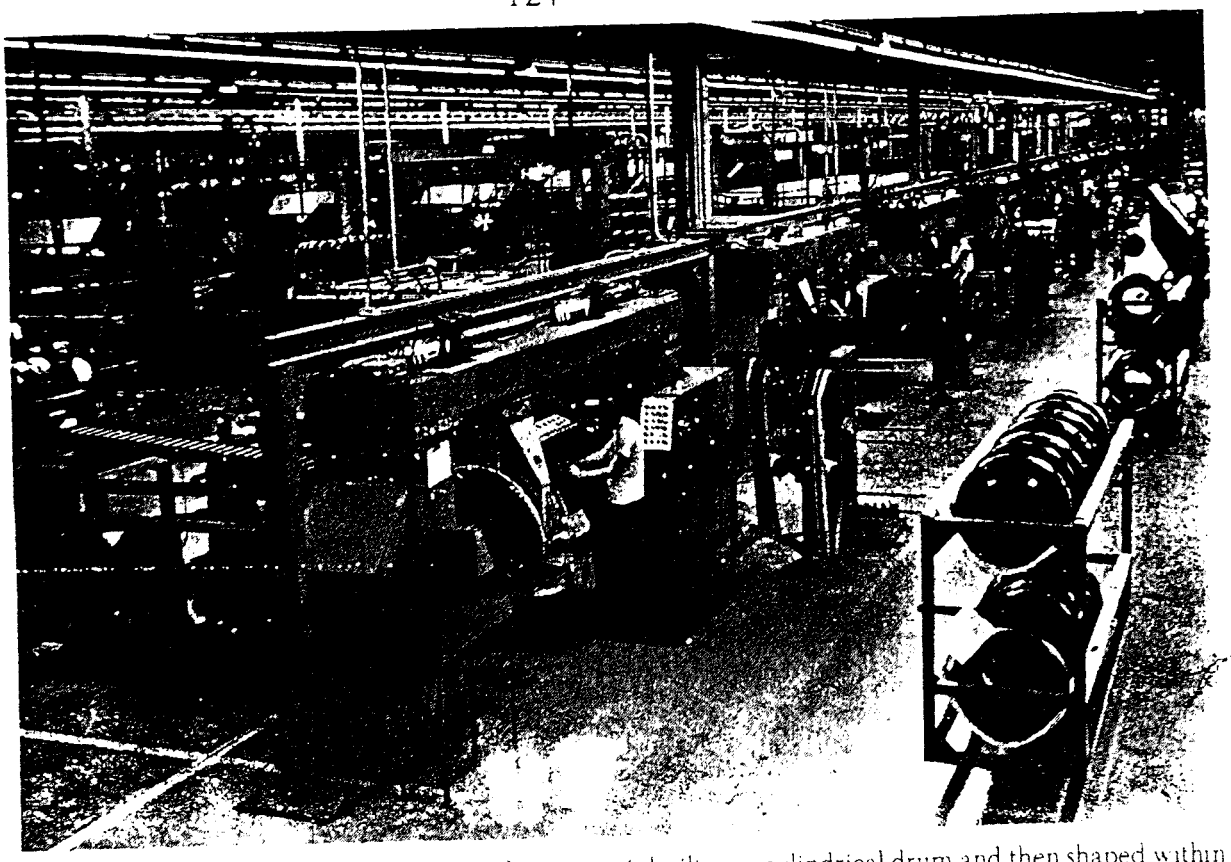

Fig. 36.9. Radial-tire building machine. The carcass is built on a cylindrical drum and then shaped within the tread and bell. *(General Tire and Rubber Co.)*

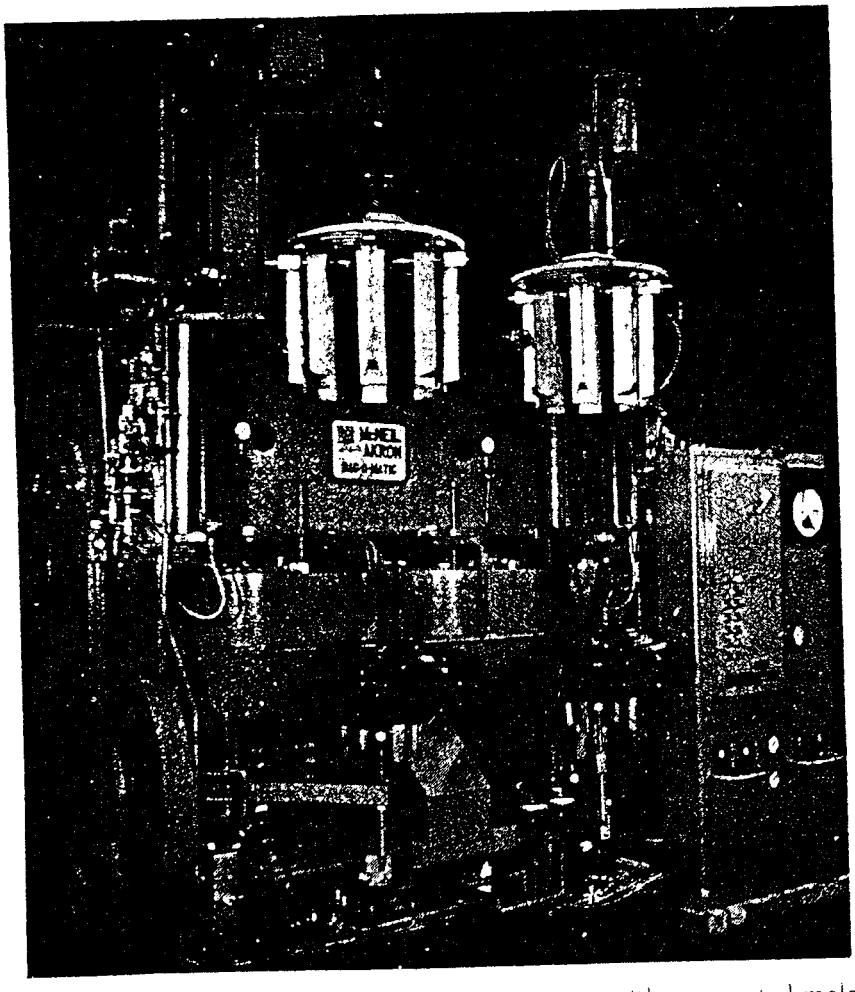

Fig. 36.10. Twin Bag-o-matic tire curing press with segmented-mold operating cylinders. Radial tires are shaped to approximately their final appearance and vulcanized in molds such as these.

tion and another layer in another direction. The beads—wire cables embedded in a tough, hard rubber—are "stitched" to the tire by folding the end of the cord fabric over. Last, the tread formed by extrusion is laid on, and the ends lapped together. The tire-building drum is collapsed, and the cylindrical tire removed and placed in a press. Here an inflatable rubber bag, usually made from butyl rubber and on a movable stem, is blown up inside the tire; the press mold is simultaneously closed, and the tire becomes a doughnut. Heat is applied through the mold and by steam inside the bag. Excess rubber escapes through weep holes and, after a timed cure at preselected temperature, the tire is formed. Present-day tires may be tubeless, with the air-retentive layer built in, or an inner tube extruded from butyl rubber may be used. Butyl rubber, although a very "dead" rubber, has outstanding resistance to passage of air. The modern automobile, in addition to tires, uses rubber in window channels, weather-strip, wiper blades, motor mounts, cushions, and sound deadening, to the extent of about 115 kg of rubber per vehicle.

Radial tires require a different method of assembly from the traditional bias cord tires as shown in Fig. 36.8. Belts of rayon, polyester, fiberglass, and steel are all being used.

LATEX COMPOUNDS

Concentrated latices permit the use of rubber as a liquid which may be spread, painted, dipped, or whipped into a foam. Suspensions of compounding ingredients provide cure, but reinforcement is not nearly as effective. The use of latex is increasing, although the foam mattress, pillow, and upholstering trades have veered toward polyurethane and polyether rubbers for their supply.

RECLAIMED RUBBER

Reclaim is a useful compounding ingredient produced from scrap rubber goods.[19] Articles are ground finely, and rubber, fabric, metals, etc., separated by combinations of chemical, mechanical, and solution methods. Reclaimed rubber is partially depolymerized and contains a high percentage of carbon black (or other pigment), ash, and solvent oils. It imparts some desirable processing character to rubber compounds but is usually used as a cheap scrap material for very cheap products. Worldwide, only about 10 percent of new rubbers are reclaimed.

The recent increased cost of energy has spurred interest in using tire waste as fuel. The burning of 1 kg of rubber produces 7.17 MJ compared with 5.26 MJ for coal. Chunks of old tires have also been mixed with asphalt to produce an asphalt-road aggregate which has many advantages over ordinary asphalt. This Swedish process, called Plus-Ride in the United States, produces roadways that last more than four times longer, have increased traction and lower noise and glare than regular asphalt roadways.

RUBBER DERIVATIVES

Rubber, particularly natural rubber, has been used as a raw material for chemical reactions to yield various derivatives of altered nature. Plastic technology is displacing these rubber-

[19]Paul, Reclaiming Rubber, *CHEMTECH* 9 (2) 104 (1979); *Chem. Eng. News* 58 (19) 22 (1980); *Chem. Week* 128 (23) 18 (1981).

based chemicals, for rubber is obviously an expensive raw material. Halides react with rubber, adding at the double bonds, to form chlorinated rubbers (or bromide and iodide may be used) which are useful as paint ingredients and are resistant to chemical attack. The action of hydrogen chloride on a benzene solution of rubber produces rubber hydrochloride, decidedly different from rubber in many ways. A tough, transparent plastic, it forms films used for packaging. Rubber hydrochloride is resistant to chemical attack, forms excellent thin films, and is colorless, odorless, and tasteless. PVC, polyethylene, polypropylene, and newer plastics are limiting the use of expensive rubber hydrochloride. Rubber and resin blends are widely used, the rubber adding its peculiar properties of impact resistance, extensibility, and resilience.

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PART 2

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Chapter 1

Energy, Fuels, Air Conditioning, and Refrigeration

As a rule, a chemical engineer is not enough of a specialist to be capable of adequately designing plants for power production, refrigeration, or air conditioning. Since the chemical process industries consume more than one-third of the energy used by *all* the manufacturing industries, chemical engineers should be familiar with the broad technical aspects of energy production and use. They should also be prepared to work with power, refrigeration, and air conditioning engineers for the proper coordination of the production of these essential tools and their use in chemical processes in order to obtain the cheapest manufacturing cost. Frequently, the cost of energy, particularly if it is to be used electrochemically, is the deciding factor in choosing the location of a factory. Process industries under the direction of chemical engineers are in most instances large consumers of steam for evaporation, heating, and drying. Consequently, these industries need large quantities of low-pressure steam. Occasionally, however, certain exothermic reactions, such as the contact sulfuric acid process, can be employed to generate steam and electricity for external use. If a steam power plant is to be used only for electrical power generation, the turbines are run condensing; if, on the other hand, both electricity and low-pressure steam for heating are needed, it is economical to lead the high-pressure steam directly from the boiler through noncondensing turbines. This uses the turbines as power-producing pressure reducers and yields exhaust steam from the prime movers to supply low-pressure steam for drying, evaporation, or other heat-users throughout the plant.

ENERGY

The increased worldwide consumption of energy has led to a search for new energy sources for the future, and this has become one of the foremost objectives of science, engineering, and government.

It is estimated that in 1850 coal, oil, and gas supplied 5 percent of the world's energy, and the muscles of humans and animals, 94 percent. Today, coal, oil, gas, and nuclear sources account for approximately 94 percent, water power about 1 percent, and the muscles of humans and animals the remaining 5 percent. Of the total amount of coal, oil, and gas that has been burned for the benefit of humans up to this time, less than 10 percent was burned

in all the years prior to 1900, and 90 percent in this century. Humans have become energy-hungry. The U.S. Navy's Admiral Hyman G. Rickover has stated this clearly:

> Our country with only 5 percent of the world's population uses one-third of the world's total energy input; this proportion would be even greater except that we use energy more efficiently than other countries. Each American has at his disposal each year energy equivalent to that obtainable from 5 tons of coal. This is six times the world's per capita energy consumption. With high energy consumption goes a high standard of living. Thus, the enormous energy from fuels feeds machines which make each of us master of an army of mechanical slaves. Man's muscle power is rated at ⅛ horsepower continuously. Machines furnish every American industrial worker with energy equivalent to that of 244 men, while the equivalent of at least 2000 men push each automobile along the road, and every family is supplied with 33 faithful household helpers. Each locomotive engineer controls energy equivalent to that of 100,000 men; each jet pilot (that) of 1 million men. Truly the humblest American enjoys the services of more slaves than were once owned by the richest nobles, and lives better than most ancient kings. In retrospect, and despite wars, revolutions, and disasters, the 100 years gone by may well seem like the 'Golden Age.'

Most energy generation involves the conversion of some type of fuel, usually by combustion. Temperature is the driving force for energy conversion, so it is usually an important variable. Table 4.1 indicates the approximate continuous temperature associated with various conversion processes.

PROJECTED ENERGY DEMANDS

There are many study groups whose function is to predict the future demand for energy. One of these, The National Petroleum Council, initially projected U.S. energy consumption to increase at an average rate of 4.2 percent per year between 1971 and 1985. This value proved

***Table* 1.1** High-Temperature Sources

Source	Temp., Continuous, K	Remark on Temperature
Bunsen burner	1400	
Blowtorch	1900	
Controlled nuclear reaction	3000	Limited by construction materials
Oxyacetylene flame	3380	Hottest low-cost chemical flame available
Combustion of aluminum powder in pure oxygen	3800–4400	Theoretical maximum; pressure 0.1 and 1 MPa, respectively
Solar furnace	4000	Maximum estimated
Combustion of carbon subnitride	5000–6000	Maximum estimated
Electrical induction furnace	to 5000	Limited by crucible construction materials
Plasma arc	2000–50,000	Depends on arc type and current

SOURCE: *Ind. Eng. Chem.* 55 (1) 18 (1963).

to be much too high. Balzhizer[1] reviewed the predictions made by various professional groups and showed that as a result of the unforeseen extraordinary price changes brought about by the Organization of Petroleum Exporting Countries (OPEC) and U.S. government restrictions on burning high-sulfur fuels, such predictions have become largely meaningless at this time. Brown[2] has also observed the failure of recent predictions and notes the effect on demand of severe changes in price. Figure 1.1, which is based on several sources, shows actual energy consumption in recent years and indicates reasonable predictions for the future. Because industry is becoming far more energy-efficient, such predictions must be regarded with suspicion. Making future plans for the production and use of energy has become very questionable.

Conservation

Energy had been kept artificially cheap in the United States until the drastic OPEC price rise and the increasing ratio of imported oil to domestic oil forced U.S. prices to approach world levels.

Space heating, transportation, and industry are the major users of energy. Industry has responded rapidly to the huge increases (nearly tenfold between 1973 and 1981) in energy costs, reducing its energy consumption yearly while the gross national product continued to increase. Figure 1.2 shows the interesting trend in industrial use of energy. Transportation has been far less responsive to prices, although the effect of smaller, fuel-efficient cars is just now beginning to show. Space heating, residential and commercial, will require considerable capital investment and new and innovative design to reduce requirements markedly; these will be slow in coming, although some slight improvement has already appeared. Conservation at all levels is absolutely essential if prices are to be maintained at any reasonable level.

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[1]Balzhizer, U.S. Energy Prospects, *Chem. Eng.* 89 (2) 74 (1982).

[2]Brown, The U.S. Energy Outlook through the Year 2000, *Chem. Eng. Prog.* 77 (9) 9 (1981).

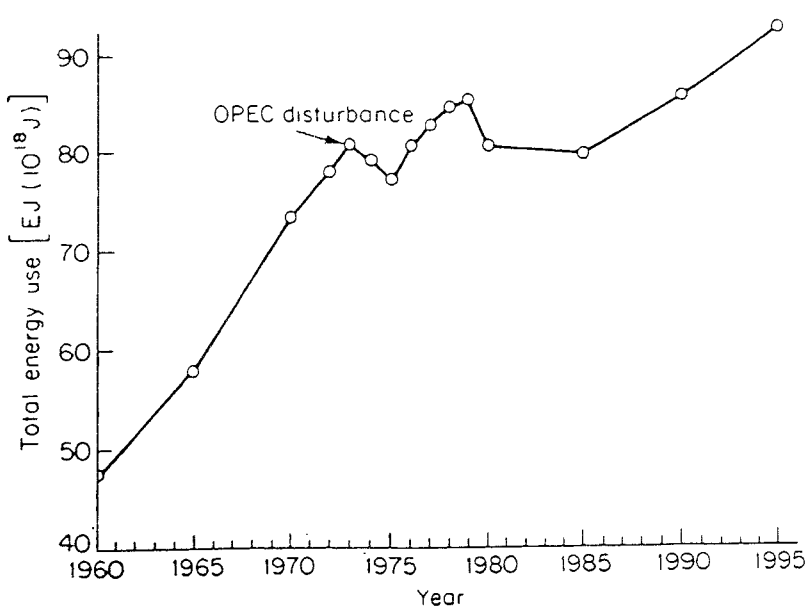

Fig. 1.1. U.S. energy consumption.

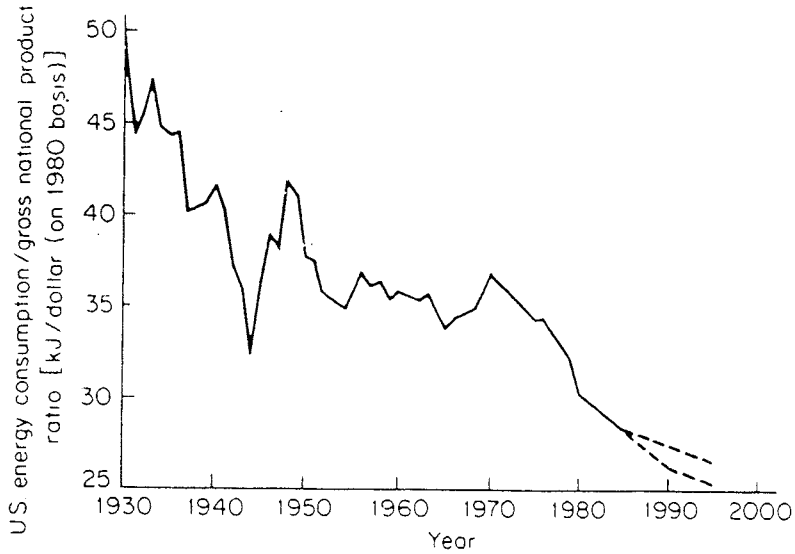

Fig. 1.2. Energy consumption ratio against gross national product, in 1980 dollars

Competitive Energy Sources

Fossil fuels and geothermal, wind, solar, tidal, human, animal, and nuclear energies are all competitive so local conditions may make one of them superior. Energy must be generated or collected inexpensively for broad general use, and Table 1.2 is an attempt to estimate costs relative to coal as of 1982. Many alternate forms of energy are of small interest because of the large investment required for a slow and erratic return. Some are inconvenient to the users or are unreliable.

FOSSIL FUELS

Fossil fuels are solids, liquids, and gases. Prices vary locally depending on abundance and competition. Competition is distorted by environmental considerations and particularly by government regulations. The abnormally low price of natural gas, regulated by the U.S. government, has led to the use of this fine, clean-burning fuel for uses for which less desirable fuels, such as coal and residual oil, would have been equally suitable. Major effort is now being expended toward better methods of coal combustion (fluidized bed combustion in the presence of limestone, flue gas scrubbers, and other pollution control systems) which result in less contamination of the atmosphere. The desire to reduce sulfur oxides in the air has led to regulations reducing the use of high-sulfur residual oils and eastern coals, however.

Solid Fuels

PEAT. Peat (wet, partially decomposed organic matter) deposits are worked in other parts of the world, but are unlikely to become a significant power source in the United States because the energy content per unit of weight is not great, deposits are mainly in isolated areas, and the drying problem is severe. There are extensive horticultural uses for peat.

***Table* 1.2** Cost of Energy for Home and Transport Use

Source of Energy	Price, $/GJ
Bituminous coal	4.3
Fuel oil	6.2
Crude oil	6.2
Natural gas	4.5
Biomass, direct combustion	1–3
Peat	1–3
Syncrude from tar sands	4.3
Producer gas	2–5
Biogas	2–12
Charcoal	5–13
Shale oil	4.3–6.1
Ethanol from biomass	15.9–32.7
Methanol from biomass	12.9–23.8
Vegetable oils	24.8–59.5
Geothermal	1.5–2
Passive solar	1
Solar panel	1.6
Solar flat plate collector (30 to 90°C)	5–20
Nuclear	5.5
Wind	Insufficiently developed to estimate, dominated by fixed charges of $200–$600 per kilowatt of installed capacity
Water power	Varies widely, generally very low. Dominated by fixed charges

LIGNITE.[3] Lignite is a fuel intermediate in composition between peat and coal. Large, accessible deposits occur in South Dakota, and there are significant deposits in seven other states. Estimated reserves are 4.07×10^{11} t representing 59 percent of the present bituminous coal reserve and 104 percent of the subbituminous reserve.[4,4a] This material is not widely used at present, although a commercial barbecue briquette[5] process is based on it, but it is potentially of great value. Some lignites contain significant amounts of uranium.

COAL. Coal is the most important of the solid fuels. Worldwide consumption is about 4×10^9 t/year with the United States consuming 7×10^8 t/year. Sufficient known U.S. reserves exist to satisfy domestic requirements for at least 200 years at the present rate of consumption, but much of this is high-sulfur coal, which causes serious air pollution. Unless the coal can be treated before, during, or after burning to reduce sulfur emissions, it cannot be used by electrical utilities or for domestic heating on a large scale. Chemical engineers continually hope that the annual shortage of oil (approximately 3×10^8 t/year) can be alleviated by the conversion of coal through commercial liquefaction and/or gasification of coal.[6] The size of such a project is extremely large, requiring creation, at gigantic expense, of an industry approxi-

[3]Mannon, Lignite Revival Takes Texas by Storm, *Chem. Eng.* 85 (7) 75 (1978); Parkinson, How to Get Water Out of Lignite, Wood, and Peat, *Chem. Eng.* 85 (7) 77 (1978).

[4]*Minerals Yearbook 1972*, Dept. of the Interior, 1974.

[4a] t = 1000 kg.

[5]*Chem. Eng.* 70 (15) 108 (1963).

mately the size of the present petroleum industry. Nevertheless, it may be done. The U.S. government is financing several small demonstration units. Here, small refers to units far larger than most chemical plants, but still small for such a huge job. South Africa has a functioning coal-to-oil business well established (Sasol).

Coals are classified, according to their fuel properties, as anthracite, bituminous, subbituminous, and lignites with subdivisions for each type. Anthracite was a valuable domestic fuel because of its clean burning characteristics, but it is now largely exhausted. The principal uses of bituminous coal are combustion for energy and carbonization (Chap. 2) for coke, tar, coal chemicals, and coke-oven gas. Table 2.1 outlines the various fields in which coal is an important raw material and the areas in which exploratory development is being undertaken. Gasified coal, as methane, low heating value gas, or high heating value gas, shows much promise as a fuel of the future and is essentially nonpolluting.[7]

Pulverized coal has been increasingly used during recent years in suspension firing for power plant installations because of the high thermal efficiency with which it can be burned, the low cost of operation and maintenance, and its great flexibility. All these factors more than balance the increased cost of preparing the fuel. In burning pulverized coal, the fly ash leaves the boiler and is carried along with the waste gases. It is removed from the flue gases by an electrostatic precipitator or other device. It has been used in bricks, building blocks, and concrete. Large tonnages of fly ash are sintered to produce a lightweight aggregate. Normally it is considered a low-valued nuisance.

COKE. Coke is a fine fuel, but it is expensive for industrial use except in blast-furnace operation, where it is a chemical reactant as well as a fuel. Coke production still parallels pig-iron production, though the amount of coke used per ton of iron continues to decrease. Other solid fuels such as coke breeze (finely divided coke dust), wood, sawdust, bagasse, and tanbark are used where they are available cheaply or where they are produced as by-products.

Liquid Fuels

FUEL OIL. The only important liquid fuel used for power generation is fuel oil. It is the fraction of petroleum crude oil that cannot be converted economically by the refiner into higher-priced products. It consists of a mixture of the liquid residues from the cracking processes and fractions with a suitable boiling point obtained by the distillation of crude oil. Fuel oils are classified by their properties, e.g., flash point, pour point, percentage of water and sediment, carbon residue, ash, distillation temperatures, and viscosity. These properties are determined by standardized tests developed under the auspices of the ASTM (American Society for Testing and Materials). The flash point indicates to a degree the safety in handling, but is relatively unimportant for determining the combustion behavior of the fuel in the burner. Oil-burning equipment usually shows higher thermal efficiency (75 percent) than coal-burning boilers and labor costs are usually less. Oil contains much more hydrogen than coal. This hydrogen burns to form water, which carries much heat out of the stack because of the high latent heat content of steam. Stack losses are nearly double those from coal combustion.

OTHER LIQUID FUELS. Other liquid fuels include tar, tar oil, kerosene, benzol,[8] and alcohol, which are consumed to a much smaller extent than fuel oil. Gasoline is consumed mainly in internal combustion engines.

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[7]Whitaker, Coupling a Gasifier to a Combined-Cycle Plant, *EPRI J.*, p. 22, April 1981.

[8]The common commercial name for technical grade benzene.

Table 1.3 shows the world energy consumption and the distribution of fuels used throughout the world. The United States used 28 percent of world production of energy in 1978.

Table 1.4 shows that the United States now has a very great dependence on the Middle East for oil to supplement its domestic production of petroleum products. The 1973 to 1974 embargo was followed by a huge increase in petroleum prices. The adverse effect of this unprecedented rise and the currently unsolved problem of imbalance of payments with the Middle East continues to depress business in the United States. The effect on developing countries has been even more severe. The energy resources of the United States are considerable, but a comprehensive energy policy has not yet been formulated by the federal government despite publication of a stated policy. The direction which is to be taken to make us once again self-sufficient in energy is not now apparent. It is well-recognized that there is not an endless supply of so-called low-cost oil. Increased crude oil producing capacity will be more costly, since much of the producing capacity will come from offshore and arctic regions involving higher costs of exploration, production, transportation, and meeting stringent environmental standards.

U.S. production of crude oil and natural gas is expected to diminish slowly over the long term. Over the middle term, some scientists feel there is much yet to be discovered by searching in new areas and at greater depths. Superior techniques for recovering oil from spent fields and new scientific methods of prospecting for oil and gas are helping to slow the downward trend. Environmental objections to the use of high-sulfur fuels as well as a hardening of the public attitude toward nuclear power generation make decision making very difficult.

Proven oil reserves have been shrinking in recent years and U.S. crude production has been falling at the rate of about 3 percent per year. Even the opening of the great Alaskan fields has not greatly slowed this fall. Best optimistic estimates, taking into account new prospecting techniques and increased drilling activity, project declines of at least 1½ percent per year.

***Table* 1.3** World Energy Consumption, 1960–1979
(in metric tons of coal equivalent)

Region and Energy	Consumption (10^6 t)					
	1960	1970	1975	1977	1978	1979
United States	1447	2204	2284	2435	2452	2506
Western Europe	787	1303	1413	1492	1526	1576
Japan	96	315	354	383	381	431
Centrally planned economies*	1254	1824	2347	2597	2725	2819
Rest of world	435	866	1131	1261	1311	1374
World total	4019	6512	7529	8168	8395	8706
Energy Source						
Solid fuels	2049	2272	2397	2560	2612	2738
Liquid fuels	1293	2792	3348	3692	3768	3834
Natural gas	593	1293	1561	1666	1738	1846
Electricity	85	155	223	250	277	288

*Includes China, Dem. People's Rep. of Korea, Mongolia, Vietnam, Algeria, Bulgaria, Czechoslovakia, German Dem. Rep., Hungary, Poland, Romania, and U.S.S.R.

SOURCE: Statistical Abstract of the United States.

***Table* 1.4** U.S. Foreign Trade in Petroleum Products, 1960–1980* (in PJ, 10^{15} J)

	Crude Oil			Petroleum Products			Natural Gas		
Year	Imports	Exports	Net Trade	Imports	Exports	Net Trade	Imports	Exports	Net Trade
1960	2,316	19.0	−2,297	1900	435	−1465	170	12.7	−157
1965	2,799	6.3	−2,793	2899	407	−2496	497	28.5	468
1970	2,968	30.6	−2,938	4911	548	−4363	892	75.9	−816
1972	4,970	1.0	−4,968	5893	493	−5400	1100	84.4	−1020
1974	7,800	6.3	−7,793	6045	483	−5562	1039	82.3	957
1976	11,855	17.9	−11,836	4677	477	−4200	1042	69.6	972
1977	14,796	111.8	−14,684	4987	430	−4557	1094	59.1	1035
1978	14,198	353.3	−13,844	4603	456	−4147	1050	55.9	−993
1979	14,583	524.2	−14,058	4333	533	−3800	1371	59.1	−1312
1980	11,710	634.9	−11,075	3566	584	−2982	1087	59.1	−1028

*Calculated from data in *Statistical Abstract of the United States*, 102 ed., 1982.

The fact must be faced that oil is a finite, nonrenewable resource and will ultimately be exhausted, possibly within the lifetime of persons already born.

SHALE OIL.[9] Shale oil has a potential to replace some of the petroleum being used, and the United States has large reserves. The oil in shale is chemically bound and cannot be simply solvent extracted. The U.S. Geological Survey has estimated mineable shale reserves at 1.77×10^{11} t of oil, sufficient to meet domestic consumption at the present rate for several hundred years. Small shale oil plants have been built and commercial-sized ones planned, but problems, economic and technical, are formidable. Only around 11% by weight of the shale is oil, and this oil, called kerogen, is somewhat inferior in quality to the usual petroleum crude oil. Until plants producing about 14,000 t of oil per day are constructed, shale processing does not approach petroleum refinery sizes and no plants of this size are currently projected. Unfortunately, shale oil deposits are mostly on public lands, in arid regions far from markets. Development[10] requires investments in the several billion dollar range, and environmental problems of considerable complexity accompany the disposal of the large volume of spent shale. This is, however, a resource that may be developed soon.

TAR SANDS. Tar sands contain up to 18% heavy bitumen entrapped in a matrix of sand, silt, and water. The light oil content of such sands averages less than that of oil shale, but recovery is much easier. Recovery is usually by steaming. Large deposits containing up to 14% bitumen have been identified and are being commercially developed. Athabasca (Canada) sands are estimated to contain 4.53×10^{11} t of recoverable oil. This is enough to supply the total energy requirements of the United States for 18 years at the 1980 consumption rate. Mining and removing the bitumen (tar) in an environmentally acceptable fashion under arctic conditions is proving to be difficult and not very profitable, but is proceeding.

Gaseous Fuels

NATURAL AND MANUFACTURED GAS. Natural and manufactured gas is burned as a source of heat in domestic installations and also in industry. Blast-furnace gas resulting from the smelting of iron is an outstanding example of a by-product gas employed for heating the blast stoves, with the remainder burned under the boilers or for heating coke ovens. Fuel gases are discussed in Chap. 3, where a tabulation of heating values and other properties is given.

The reserves of U.S. oil and gas are not inexhaustible. The cost involved in finding, developing, and supplying oil and gas will probably increase sharply with time. Government regulations are a major influence on the supply and utilization of natural gas. Deregulation completely alters the situation.

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[9]Frumkin, Owens, and Sutherland, Alternate Routes for Refining Paraho Shale Oil, *Chem. Eng. Prog.* 75 (9) 64 (1979); Gerry, Combined Retorting Technique for Shale Oil, *Chem. Eng. Prog.* 75 (9) 72 (1979); Duir, Griswold, and Christolini, Oil Shale Retorting Technology, *Chem. Eng. Prog.* 79 (2) 45 (1983); Dougan, The BX in Situ Oil Shale Project, *Chem. Eng. Prog.* 75 (9) 81 (1979); Kaplan, Improved Routes for Making Jet Fuels from Shale Oil, *Chem Eng.* 88 (26) 39 (1981); Taylot, Oil Shale Commercialization: The Risk and the Potential, *Chem. Eng.* 88 (18) 63 (1981).

[10]McIntyre, Giant Oil-Sands Plant Comes On-Stream, *Chem. Eng.* 85 (20) 123 (1978); Kohn, Oil Recovery Is Higher in New Tar-Sands Route, *Chem. Eng.* 87 (25) 37 (1980).

Combustion

Most modern industrial plants burn coal on mechanically operated grates or stokers or in the pulverized form. These present-day procedures allow the ratio of air to fuel to be properly controlled, thus ensuring efficient combustion and reducing heat losses through stack and ash. When fuel oil is burned, it is frequently necessary to provide heaters to lower the viscosity of the oil sufficiently for proper burner operation. The flue gas analysis is valuable in controlling combustion, since the proportions of CO_2, CO, and O_2 in the flue gas will indicate incomplete combustion or excess air.

Cogeneration

Certain chemical processes such as sulfuric acid and ammonia manufacture produce a substantial surplus of heat, available usually as medium- to high-pressure steam. At present beer manufacture, paper manufacture, and oil refining are also producing surplus steam that is converted to salable electricity and useful residual thermal energy. This is not new, but the practice is growing. There are problems in collecting and utilizing diverse small sources,[11] but efficiencies of even small units can be quite high and the Public Utilities Regulatory Policy Act of 1978 makes cogeneration very attractive economically. These sources were estimated to total 6 GW with a potential for 12 GW by 1990.

POWER GENERATION

About 1800 the first successful attempt to generate steam under pressure in an enclosed vessel was made. Since then the use of steam has increased to such an extent that today steam furnishes the major portion of the power developed in the country. The most recent developments have been toward improvements in boiler construction in central power stations, with the aim of producing higher-pressure steam. Such high pressures increase overall efficiency in the production of electric power. The limiting factor is the failure of materials at the high temperatures and pressures involved. Earlier 0.569 to 0.631 kg of the best coals were required per megajoule of energy produced, whereas currently, some power plants produce a net megajoule from 0.078 kg of coal. Figure 1.3 is the elevation of a large utility water-tube boiler.

Boilers

Standard boilers are either *water* (inside the) *tube* or *fire tube*. Large high-pressure units are water tube; smaller units for lower pressure and portable units are often the simpler fire-tube units.

Water-tube boilers are usually large stationary installations that generate steam at pressures above 1000 kPa. The water is in the tubes and can be converted to steam more quickly

[11]Wayne, Plugging Cogeneration into the Grid, *EPRI J.* p. 6, July/August 1981. Roszkowski, Grisso, Klumpe, and Snyder, Gasification in Combined Cogeneration Cycles, *Chem. Eng. Prog.* 79 (1) 9 (1983).

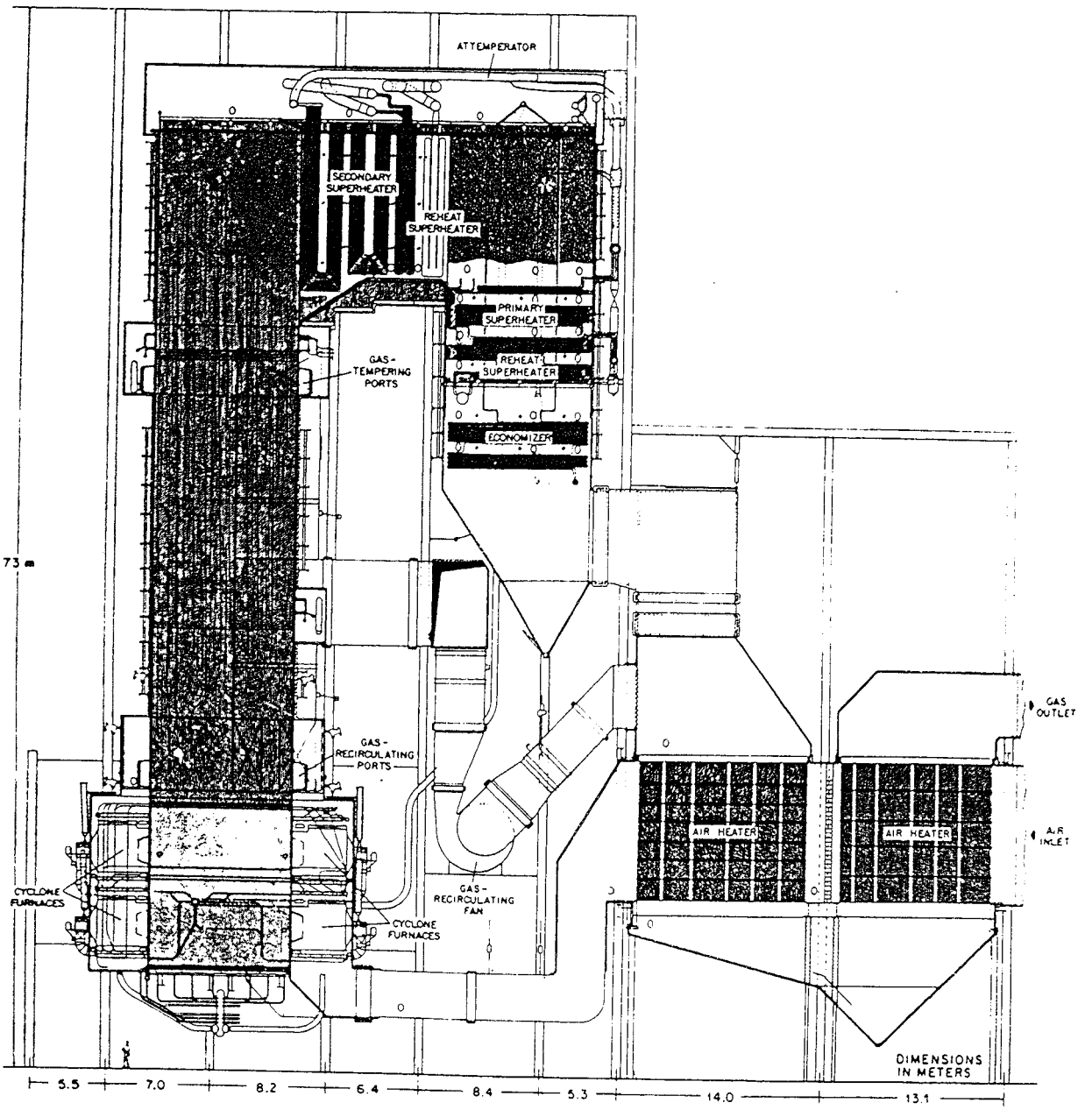

Fig. 1.3. Elevation of a large utility water-tube boiler. Capacity 2×10^6 kg/h; outlet pressure 18.1 MPa; temperature 540°C; height 73 m. *(Babcock and Wilcox Co.)*

(quicker steaming) than in a fire-tube boiler. All high-efficiency units are of this type. Boiler feedwater treatment is vital for trouble-free service. Foaming, caustic embrittlement, corrosion, and scale formation result when insufficiently conditioned water is used. Higher pressures require very carefully conditioned feedwater.

Figure 1.4 shows a portable packaged boiler that is used for generating steam at 1725 kPa and that has a capacity of 45,000 kg of saturated steam per hour.

Electric Power from Steam

Much steam is generated solely to produce electrical power. In the process industries, however, steam is used for heating vessels—usually at comparatively low pressure. This "process steam" demand is often very large in chemical manufacturing plants. Coordination and balancing the power and process steam requirements can result in major cost reduction. Large

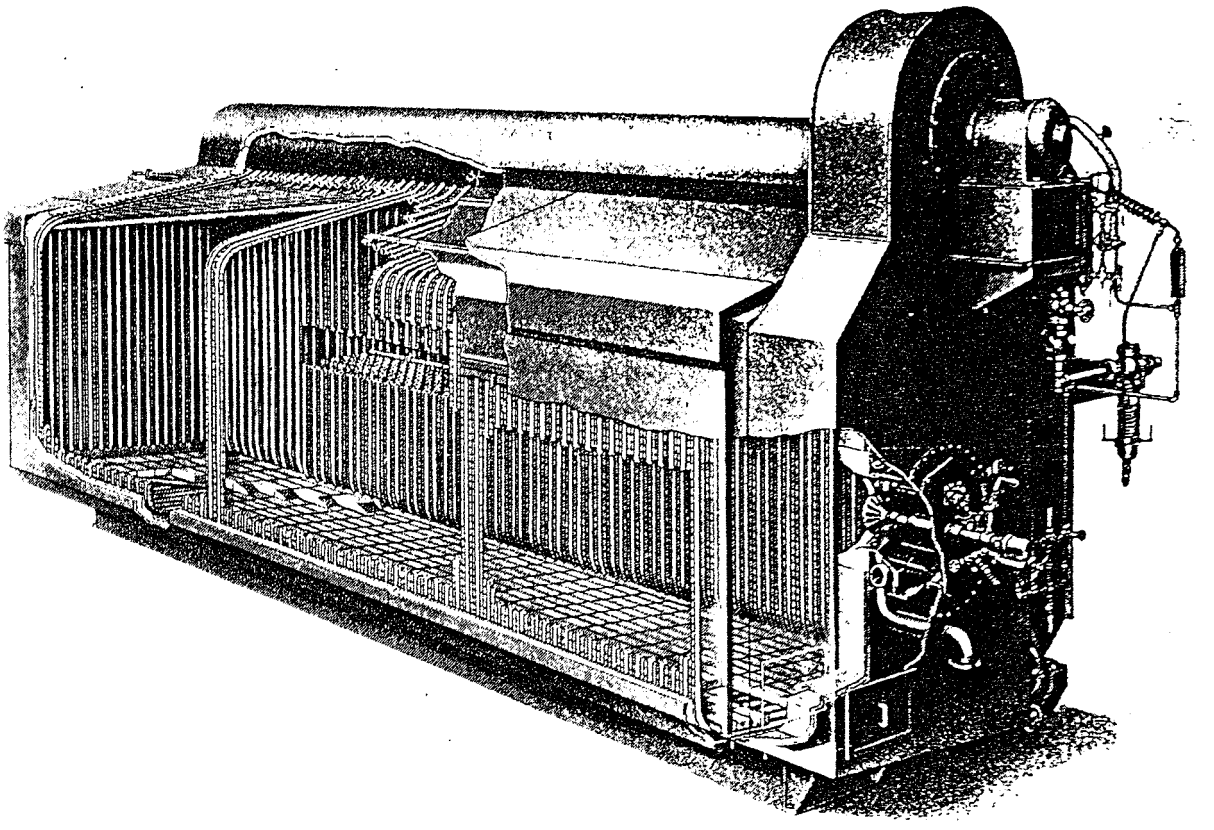

Fig. 1.4. Portable water-tube boiler *(Babcock and Wilcox Co.)*

utility generating plants generate steam at high pressures and with considerable superheat, then pass it through turbines exhausting into a vacuum produced by large condensers. This procedure extracts maximum power from the steam generated.

Superheat is very undesirable in process steam, and high pressure is usually unnecessary and unwanted. Instead of exhausting the power-producing turbine to a vacuum, saturated steam can be removed (bled off) from the turbine at the pressures and temperatures at which process steam is required. This effectively uses the turbine as an energy-efficient reducing valve. This system can save as much as 61 percent in fuel compared with a conventional system. Such systems have also been used in nitric and sulfuric acid plants to increase heat-use efficiency. One author has described a sulfuric acid plant as "a power plant that incidentally produces sulfuric acid."[12]

Balancing heat use and electrical power demand for cogeneration plants has proved to be somewhat of a problem. Superheat is necessary to prevent erosion of turbine blades, but it reduces the heat-transfer rate with process steam. Table 1.5 shows the relationship between power and heating value of steam. Turbines are ideal for chemical plants because of their flexibility as prime movers and their ability to act as efficient pressure reducers. The economies obtained by cogeneration are increasingly important in chemical process plants.

Heat Transmission Other than by Steam

Where indirect heating is necessary, some method other than steam should be used for temperatures above 200 to 230°C, where the pressure of steam becomes too high for economical

[12]Anon., The Changing Sulfuric Acid Industry, *Chem. Week* 130 (6) 40 (1982).

Table 1.5 Comparison of Energy from the Isentropic Expansion of Steam to an Exhaust Pressure of 20.7 kPa for Power and Heat-Transfer Processes

Sat'n. Pressure, kPa	Sat'n Temp, °C	Degrees of Superheat, °C	Vapor Temp., °C	Enthalpy, kJ/kg	Entropy, kJ/kg·K	End of Expansion			Work of Expansion, kJ/kg	Heat Available for Process, kJ/kg
						Enthalpy, kJ/kg	Moisture Content, %	Temp., °C		
2758	229	278	507	3475	7.293	2779	—	156	695	2273
2758	229	222	452	3354	7.135	2702	—	122	645	2200
2413	222	194	417	3275	7.084	2689	0.6	—	586	2182
2069	214	278	492	3452	7.394	2826	—	178	626	2319
2069	214	167	381	3205	7.043	2675	1.4	—	530	2168
1724	205	139	344	3128	7.009	2663	2.0	—	465	2156
1379	194	222	417	3291	7.361	2807	—	166	484	2300
1379	194	111	305	3052	6.980	2652	2.5	—	400	2145
1034	181	83	265	2973	6.967	2652	2.5	—	321	2145
690	164	111	275	3010	7.210	2745	—	138	265	2238
690	164	56	220	2891	6.988	2654	2.5	—	237	2147
345	138	111	250	2963	7.449	2845	—	188	119	2338
345	138	50	188	2838	7.193	2740	—	136	98	2233

SOURCE: Data computed from Keenan, Keyes, Hill, and Moore, *Steam Tables—Thermodynamic Properties of Water Including Vapor, Liquid, and Solid*, Wiley, New York, 1969. Superheated steam is used to prevent erosion of turbine blades caused by droplets of moisture in the steam.

design of the plant. Steam owes its importance as a heating medium to its convenience and cleanliness, but particulary to its large heat of condensation. Where conditions lie outside the range of steam, the engineer turns progressively, as the temperature rises, to other means such as:

Method	Temperature °C	Remarks
Direct firing	Above 150	Low cost and convenient but a fire hazard
Indirect firing	Above 150	Low operating cost but elaborate setting and a fire hazard
Direct gas heating	Above 150	Moderate cost and excellent control but a fire hazard
Hot oil	150–315	Good control but high first cost and oil carbonization problems
Dowtherm	204–400	Good control and moderate operating cost but higher first cost
Mercury vapor	315–650	Good control and moderate operating cost but highest first cost
Mixed salts	120–480	Good control and good heat transfer at high temperature
Electricity	Above 150	Most accurate control but operating cost usually high

Direct or indirect heating with coal or gas is frequently surprisingly efficient when the furnace is well designed; however, the open flame is a fire hazard. Under conditions where oil is not carbonized, this heat-transfer medium has been so widely employed that furnaces for heating the oil and equipment for the heat transfer are both available on the market as standardized and tested designs. Dowtherm (diphenyl 26.5%, diphenyl oxide 73.5%, eutectic mixture) is stable at higher temperatures than oil and has the added advantage that it can be employed as a vapor, where its latent heat of condensation can be used as well as its sensible heat. Other temperature-stable oils and chemicals are being used as high-temperature heat-transfer media. Mercury has been successfully used in controlling the heat of reaction in reactors, but it is extremely heavy and its vapors are poisonous.

For years mixtures of inorganic salts have been accepted as heat-transfer media, but the modern large-scale demand for such salts to remove heat from petroleum cracking processes such as the Houdry catalytic one was necessary to justify a careful study of the properties of the mixed salt consisting of approximately 40% $NaNO_2$, 7% $NaNO_3$, and 53% KNO_3. Tests indicated no danger even when a stream of hot petroleum was injected into the molten nitrate-nitrite bath. Electricity in contact, immersion, and radiant heaters is a most convenient, accurate, safe, and efficient heating medium though it is generally costly.

Nuclear Energy

There exist only two generally accepted possibilities for meeting increasing energy needs during the next 20 years, coal and nuclear fission. Both possess disadvantages that generate public concerns. For a unit of power produced, coal plants release more radioactivity than nuclear plants of similar capacity. Sulfur dioxide pollution is believed to be the cause of "acid rain" (precipitation with a low pH due to air constituents). Some lakes show recent decreases in pH believed due to such acid rain. Nuclear power is nonpolluting, but the absence of visible and tactile effects causes great concern in some quarters. Harm to human beings as a result of

nuclear power plant emissions has not yet been reported. Proven uranium reserves are sufficient to last until the turn of the century if used in fission reactors on a once-through basis. Breeder reactors increase the recovery by a factor of at least 100, making the supply of fissionable material sufficient for power demands for 100,000 years if all possible fuels are properly used and recycled.[13] The National Academy of Sciences has recommended that "national policy should support the continued use of nuclear power for the next few decades."

The United States led the world into the nuclear age, but vascillating public policy and objections by vociferous minorities have caused it to fall behind other countries in adopting nuclear power production and have put the whole domestic nuclear program in doubt. Twelve percent of domestic power, equivalent to 2.08×10^5 m^3 of oil per day, was derived from nuclear fission in 1980.[14] It is difficult to see how the country can meet its immediate needs without using nuclear power.

Worldwide nuclear power is a major source of energy, and its production is rapidly increasing. The United States is not able to set world policy, so nuclear power will probably develop rapidly on a worldwide scale without U.S. influence. As of 1981, 241 nuclear power plants were in commercial operation, and 535 more were either under construction or authorized. These plants will produce 408,100 MWe, 244,600 outside the United States. Table 4.6 shows the current distribution of power plants.

Hydroelectric Power

Many chemical industries require large amounts of low-cost electrical power for their operations. Hydro power, developed in times when capital and interest costs were low, is frequently very inexpensive, but most large sources in the developed countries have been exploited, and small units produce electricity at higher cost. Hydroelectric plants must be situated where a head of water is available from a waterfall or a dam. This water is used to drive a turbine attached directly to a generator. The initial cost of a hydroelectric plant is much greater than that of a steam plant of identical size, but the operating cost is far lower.

OTHER POSSIBLE SOURCES OF ENERGY (Alternate Energy Sources)

Biomass

Wood, bagasse, and similar biomass[15] materials have been important home heating fuels since ancient times. A few industrial operations operate on wood waste or sawdust. Despite the extreme pollution that characterizes wood combustion, it is being touted for space heating. It

[13]National Academy of Sciences, *Energy in Transition 1985-2010*, Freeman, San Francisco, 1979.

[14]*Two Energy Futures: A National Choice for the Eighties*, American Petroleum Institute, Houston, Tex., 1980.

[15]Calvin, The Sunny Side of the Future, *CHEMTECH* 7 (6) 352 (1977).

***Table* 1.6** World Nuclear Power Plants Operable, Under Construction, or On Order as of June 30, 1981

	Authorized	Operating
Argentina	3	1
Austria	1	0
Belgium	7	3
Brazil	3	0
Bulgaria	4	3
Canada	24	10
Czechoslovakia	11	3
Egypt	1	0
Finland	4	3
France	59	26
German Democratic Republic	7	5
German Federal Republic	29	11
Hungary	4	0
India	10	4
Italy	9	4
Japan	35	13
S. Korea	9	1
Libya	1	0
Luxemborg	1	0
Mexico	2	0
Netherlands	2	2
Pakistan	1	1
Philippines	1	0
Poland	2	0
Romania	3	0
South Africa	2	0
Spain	18	3
Sweden	12	8
Switzerland	7	4
Taiwan	6	2
United Kingdom	42	32
United States	172	72
U S S R	41	29
Yugoslavia	1	1
World total	535	241
Non-U S	363	1169

is doubtful that any large-scale use of biomass materials can come about, particularly because the land that would be used for its growth is more desperately needed for agriculture.

Geothermal Energy

While the present applications of geothermal energy make only a small contribution to the world's total energy generation, there were 85 units in operation[16] in 11 countries in 1981. These had an installed capacity of 1759 MW with 1830 MW more planned or under construction for completion in 1982. Iceland, Italy, Mexico, New Zealand, and the United States have commercial stations operating. The largest has a capacity of 500 MW. Several types of units have been devised and operated, including a dual-binary system using isobutane and propane as the secondary fluids. The techniques are well established, but as yet geothermal fields with extensive enough areas to be widely useful as proven sources have not been delineated.

Wave and Tidal Energy

In areas where large tides occur, the possibility of producing modest amounts of power exist. The French have created a successful operating unit. Low head and intermittent operation makes such units unattractive. Invention of a high-density cheap storage system could help in the development of tidal, solar, and wind energy. Wave energy awaits development of effective and efficient energy transducers.

Fuel Cells

These devices, which generate electricity without moving mechanical parts, have very interesting possibilities. Their theoretical possibilities have been understood for a long time, but practical units have become possible only recently, and even today the requirement of very clean fuel limits their scope. A fuel cell is a device substantially without moving parts, in which a fuel, such as hydrogen, natural gas, methanol, or propane, can be converted directly into twice the quantity of electrical energy that would result from the usual boiler-turbine-generator combination. Efficiencies are 40 to 80 percent, versus the usual 25 to 40 percent.

The fuel cell differs from the storage battery in that usually its gaseous or liquid fuel and its oxidizer are led in from outside, whereas the storage battery stores its solid fuel and oxidizer on plates where they are consumed. A fuel cell[17] operates electrochemically or, more literally "chemicoelectrically," as shown in the cell diagrammed in Fig. 1.5. This cell is actually a reactor wherein hydrogen as the feed stream or fuel is conducted into the empty space paralleling the porous, electrically conducting anode. This anode can be made of porous carbon with a metal catalyst such as platinum, which chemically changes the hydrogen atoms to positively charged hydrogen ions and electrons. The electrons leave the anode, perform

[16]DiPippo, *Geothermal Energy as a Source of Electricity,* Supt. of Documents Stock No. 061-00-00390-8, 1980; There's a Boom in Geothermal Power, *Chem. Week* 130 (26) 29 (1982).

[17]Sweeney and Heath, *Fuel Cell: Its Promise and Problems,* API, Houston, Tex., May 9, 1961, Parkinson, Fuel Cells' Prospects Are Getting Brighter, *Chem. Eng.* 90 (2) 30 (1983).

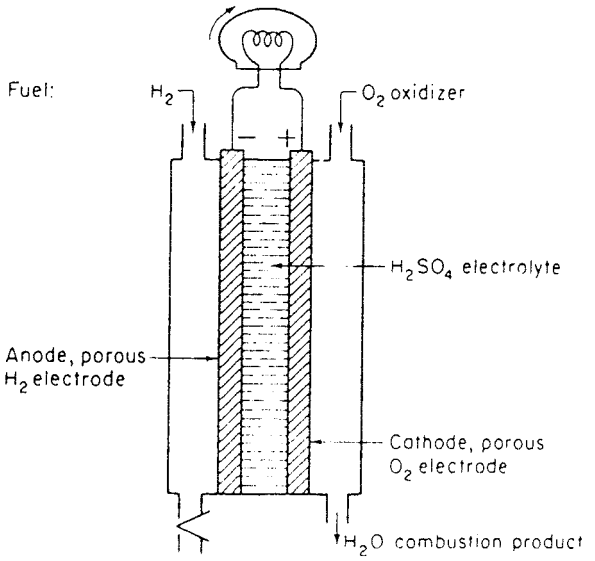

Fig. 1.5. A hydrogen-oxygen fuel cell in which the current is carried internally via mobile hydrogen ions. (Sweeney and Heath[17])

work, and enter the cathode (Fig. 1.5). Meanwhile the positively charged hydrogen ions migrate through the electrolyte (for instance, 50% KOH or H_2SO_4) attracted by the oxygen from the cathode. To complete the reaction, the oxygen pulls in the electrons also, and water is generated and discharged from the cell. The cell is so arranged that the electrons must move up the anodes, leave the cell through a wire, and enter the cell again at the cathode. While the electrons are outside the cell, they form the electric current and do work.

$$H_2 \xrightarrow{\text{anode}} 2H^+ + 2e$$

$$O_2 \xrightarrow{\text{cathode}} 2O$$

$$2H^+ + O \text{ (or } \tfrac{1}{2}O_2) + 2e \rightarrow H_2O$$

Cell overall:

$$H_2(g) + \tfrac{1}{2}O_2(g) \xrightarrow[2 \text{ electrons}]{25°C,\ 101\ kPa} H_2O(l) \qquad \Delta E = -237 \text{ kJ}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \xrightarrow{25°C,\ 101\ kPa} H_2O(l) \qquad \Delta H = -286 \text{ kJ}$$

$$\text{Theoretical efficiency} = \frac{237}{286} \times 100 = 82.9 \text{ percent.}$$

The decrease in free energy indicates that the hydrogen and oxygen will react more readily; the fuel cell provides a mechanism for this. Hydrogen-oxygen fuel cells have been operated at about 25°C, but a single cell produces about 1 V of direct current, so many cells are needed in series to produce useful voltage.

In many places in the United States it is much cheaper to use natural gas or propane in fuel cells than to purchase generated electricity. It is also much cheaper to use air rather than oxygen for the oxidizer. Many other chemicals are being studied for use in fuel cell operation. One form of current interest uses the oxidation of methanol to formic acid. The questions to be resolved are relative costs and the actual design of an efficient cell. The fuel cell is one of the most interesting devices for the production of useful energy now being investigated.

Figure 1.6 shows an example of a commercial fuel cell that achieves an efficiency above 40 percent in generating electricity. If such a unit could be placed where the waste heat generated could be used for space heating (offices, apartment houses, homes), thermal efficiencies of over 80 percent could be obtained. Electrical transmission costs are also reduced when the generating system is very near the consumer. Because such units are quiet and nonpolluting, they can be placed in residential areas. A considerable number of these units are being built, installed, and tested.

Solid Waste Energy

Particularly in the United States, large amounts of trash and garbage are generated and disposal is a major problem. Several cities are now burning trash and garbage to generate steam and electricity. Results appear to be quite satisfactory, although refuse-derived fuel (RFD) has been unsatisfactory for some installations. Air pollution must be carefully avoided, but this use of waste is very desirable. Table 1.7 shows the heating value of waste materials.

[18]Porteous, *Refuse Derived Fuels*, Wiley, New York, 1981.

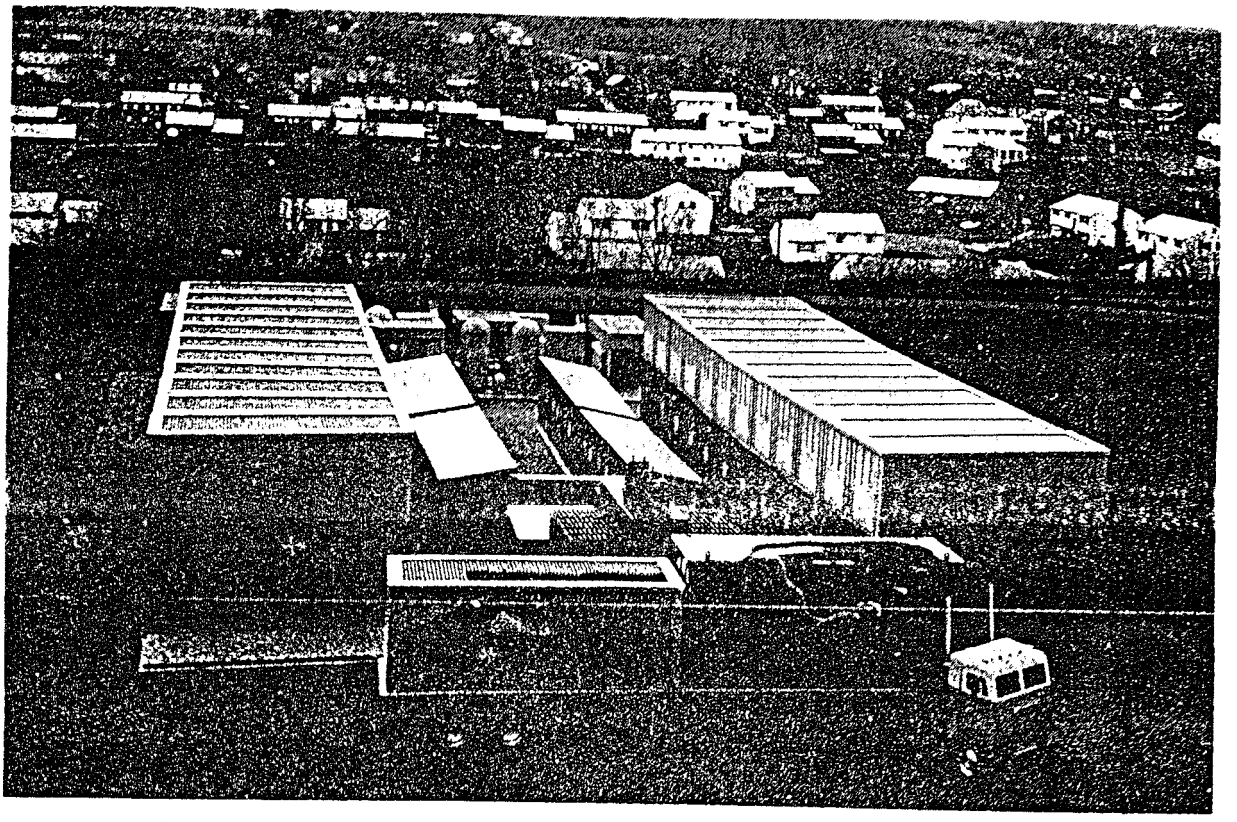

Fig. 1.6. Model of United Technologies' 26-MW dispersed generator under development for electric utility application, which was designed to generate electricity at 40 percent efficiency. It uses naphtha fuel. *(United Technologies, Power Systems Div.)*

***Table* 1.7** Approximate Heating Value and Density of Some Representative Wastes

	Heating Value as Fired, Mj/kg	Density as Discarded, kg/m^3
Bitumen waste	38.5	892
Brown paper	16.7	80
Cardboard	15.8	107
Cork	26.4	190
Corrugated paper (loose)	16.4	59
Hardboard	19.0	535
Latex	23.3	713
Meat scraps	17.7	238
Nylon	31.7	119
Paraffin wax	43.3	832
Plastic-coated paper	17.1	80
Polyethylene film	46.0	12
Polypropylene	46.2	59
Polystyrene	41.1	104
Polyurethane foam	40.9	33
Resin-bonded fiberglass	45.4	589
Rubber	34.0	713
Shoe leather	16.8	321
Tar paper	26.7	268
Textile nonsynthetic waste	18.6	166
Textile synthetic waste	34.9	143
Vegetable food waste	20.9	178

SOURCE: *Chem. Eng.* 81 (18) 38 (1974)

Biogas

Methane, produced by the decay of vegetable matter, was early identified as combustible "swamp gas." This highly desirable fuel was obtained by fermentation of sewage in Decatur, Ill. as early as 1934 and was used for heating and in internal combustion engines for pumping. Attention is currently focused on methane generation from large cattle feedlots[19] for distribution to towns; on smaller dairy farms it is being used on the farm itself. Several large demonstration plants are functioning well and many small units are in daily use. The total amount produced is small but of great significance locally.

Solar Energy

There are two serious problems that restrict the use of solar energy: it is diffuse (averaging 1 kW/m^2) and only intermittently available. There is much confusion regarding the meaning of the term "solar energy." Plants grow, winds blow, and waves are generated by the energy provided by the sun. Converters are needed to change the available solar energy into the forms usually needed by modern civilization—electricity and high-level heat.

[19]Anon., New Processes Harvest Farm Energy, *Chem. Week* 129 (15) 41 (1981).

Passive devices, such as south-facing windows, collect and effectively utilize solar heat. Active devices are being tried for concentrating solar energy to run boilers, which then produce power by conventional methods. The use of mirrors has enabled the great solar furnaces to attain very high temperatures. Photovoltaic cells convert solar energy into electricity directly. Water power and solar power are much alike in one respect: it is the large initial investment cost and the maintenance charges that offer the problem. The average roof receives more energy from the sun than the electrical energy which the house uses; the difficulty lies in the cost of capturing and converting it, storing it for use night and day throughout the year, and paying for and maintaining the expensive and complex devices. Solar cookers are quite practical in tropical countries but have never been acceptable to the cooks. Solar water heaters are quite popular on the oceanic islands, which are chronically short of fuel, and even enjoyed a brief (1936–1941) popularity in Florida,[20] but they proved uneconomical because of maintenance problems. Higher fuel costs have made solar hot water heaters again attractive, so a great many are currently being installed. It is probable that their better construction materials will make the solar heaters being installed today more attractive and competitive investments. A considerable number of new installations are taking place. For example, 8598 solar swimming pool heaters, 2910 domestic hot water heaters, 1787 space heaters, 234 space coolers, and 231 industrial processing units were installed in the United States in 1979.[21]

Photovoltaic devices are currently serving satisfactorily in watches and calculators, and as sources of electrical power for electronic devices in isolated areas.[22] The probability is quite small that solar energy will be a major source of power in this century. One major reason is that the large amount of material that must be assembled to take advantage of this diffuse source is greater than our industry could create if extensive use was made of solar power. Put another way, the amount of energy required to build the apparatus would not be recovered for many years

Ethanol from Biomass[23]

Countries with favorable growing conditions for rapid production of biomass and with major oil shortages are experimenting with ethanol as an automotive fuel. U.S. attempts to use grain-derived alcohol as automotive fuel in the 1930s foundered on high cost, difficulty of maintaining alcohol-gas mixtures, and indifference. The same difficulties exist today. A bushel of grain produces at most 9.5 L of ethanol. Ordinary distillation produces only 95% ethanol; this will not mix with gasoline unless the last 5% of water is removed, and this requires an expensive additional process. Once mixed, alcohol-gasoline mixtures separate if any water enters the system, and this is almost impossible to prevent. None of these problems exist when pure

[20]Scott, What Became of Solar Water Heating? *CHEMTECH* 11 (6) 328 (1981).

[21]*Statistical Abstract of the United States*, 1980.

[22]Solar Cells Are Getting a Big Buildup, *Chem. Week* 127 (21) 46 (1980); Davison, Harris, and Martin, Storing Sunlight Underground, *CHEMTECH* 5 (12) 736 (1975); A Shakedown Shapes Up in Photovoltaics, *Chem. Week* 130 (5) 33 (1982).

[23]Fong, Jones, and Semrau, Costs of Producing Ethanol from Biomass, *Chem. Eng. Prog.* 79 (9) 39 (1980); Emert and Katzen, Gulf's Cellulose-to-Ethanol Process, *CHEMTECH* 10 (10) 610 (1980); Biomass to Ethanol without Fermentation, *Chem. Week* 125 (22) 38 (1979).

ethanol is used as fuel, except the cost. Cellulose hydrolysis to glucose followed by fermentation appears to be more promising as a source of fuel alcohol than other options currently considered. Because much forest land is not suitable for agriculture, the use of wood would not reduce the food supply. Attempts to require 10 percent of biomass-derived ethanol in domestic gasoline are politically acceptable to grain producers but economically impossible. Brazil is engaged in major production of motor fuel ethanol from sugar cane and appears to be doing quite well.[24]

Vegetable Oils

There is no doubt whatever that a wide variety of vegetable oils can be used, particularly as diesel fuels, with little or no additional processing. Prices are extremely high, however, and most such oils now produced are needed and are more valuable as food.

Ocean Thermal

A large potential for power production exists because of the difference in temperature between the ocean surface and its depths, particularly near the equator.

These differences can be used to drive machines which can produce electricity. A small land-based plant utilizing this principle has been built on the island of Nauru[25] by the Japanese, and the United States has two small units on Hawaii. Other countries (France, India, the Netherlands) are also engaged in research projects.

Pipeline Hydrogen

Hydrogen may become an important secondary energy form if problems of generating, storage, and transportation can be solved. Like electricity, hydrogen requires some other source of energy for its production. Once produced, however, hydrogen holds the promise of significant technical and economic advantages over its competition. For example, preliminary calculations show that pipelining hydrogen should be cheaper than transporting electricity by wire. Arguments, currently unresolved, surround costs and the possibility that cheaper methods of manufacture may be possible by unconventional means.

Fusion

Although there is much talk about it, there is as yet no process that produces fusion power and no assurance that there will ever be. Ultimately, the future of humankind as an energy-using creature may depend on the development of the fusion process. Enthusiasts predict that this method will be totally nonpolluting, be free of harmful by-products, and pose low risks. Some such ideas were advanced when nuclear energy first appeared. It was said that the cost

[24]Goodrich, Brazil's Alcohol Motor Fuel Problem, *Chem. Eng. Prog.* 78 (1) 29 (1982).

[25]Kohn et al., OTEC Gets Less Funding, but Stays Afloat, *Chem. Eng.* 89 (3) 43 (1982).

of energy would become so cheap that it would be given away. Disadvantages have a way of appearing after a new process becomes commercially operative.

A nuclear fusion reactor is a device in which controlled, self-sustaining nuclear fusion reactions may be carried out to produce useful power. Such a device does not now exist. Fusion is now carried out in extremely hot but tenuous fuel gas mixtures of hydrogen, helium, or lithium isotopes.

AIR CONDITIONING

Control of temperature, humidity, and cleanliness of air is essential for human comfort in the hotter parts of the country and for the operation of many chemical processes. Artificial fiber production, certain pharmaceuticals, and photographic materials are particularly sensitive to ambient temperature. Efficient refrigeration processes combined with careful control of the humidity make the processes reasonably priced, but cooling still remains quite expensive. The design of air-conditioning units should usually be left to experts.

REFRIGERATION

Removal of heat from a substance results in its cooling. The term refrigeration is usually applied to cooling below ambient temperature. Reactors frequently require use of refrigeration. The following processes could not proceed without refrigeration: manufacture of azo dyes, freezing out isomers from each other and/or impurities, food and beverage preservation, catalytic manufacture of ethyl chloride from ethylene and anhydrous hydrogen chloride at −5°C under pressure, the production of "cold" rubber by polymerization at 5°C or lower, and the freezing of mercury at −73°C into complex molds that are coated by repeated dipping into ceramic slurry followed by melting out of the mercury. Refrigeration operations involve a change in phase of a substance so that it will be capable of abstracting heat, such as the vaporization of ammonia or the melting of ice. Mechanical refrigeration can be divided into two general types: the *compression* system and the *absorption* system. Both systems

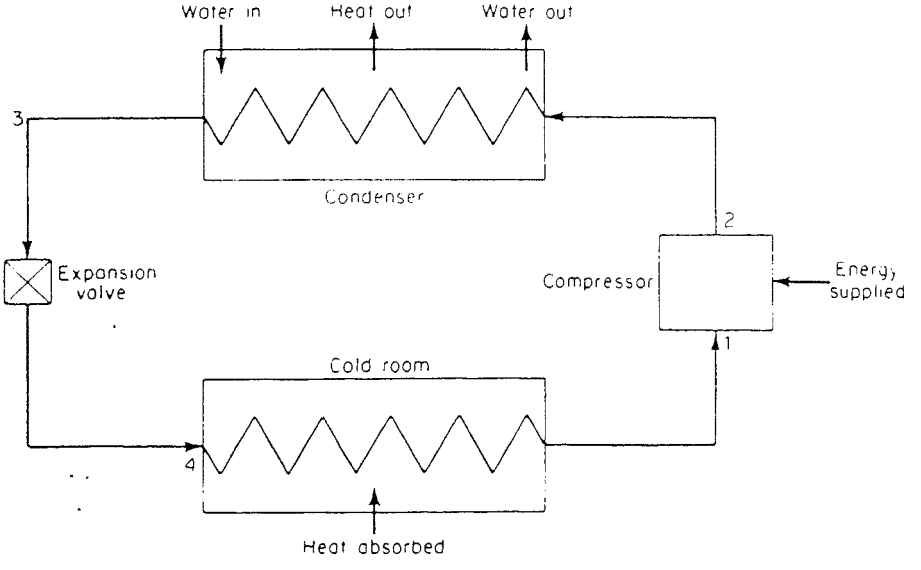

Fig. 1.7. Compression system for refrigeration

***Table* 1.8** Properties of Refrigerating Agents

Refrigerant	Boiling Point at 101 kPa, °C	Critical Temperature, °C	Critical Pressure, MPa	Latent Heat at 101 kPa, kJ/kg
Ammonia (NH_3)	−33	132	11.41	1370
Carbon dioxide (CO_2)	−78*	31	7.47	293†
Sulfur dioxide (SO_2)	−10	157	7.95	388
Methyl chloride (CH_3Cl)	−24	143	6.73	428
Ethyl chloride (C_2H_5Cl)	+13	187	5.32	391
Freon-12 (CCl_2F_2)	−29	112	4.05	167
Propane (C_3H_8)	−43	97	4.29	370

*Sublimes

†Latent heat at −29°C and 1521 kPa.

cause the refrigerant to absorb heat at low temperature by vaporization and to give up this heat elsewhere at higher temperature by condensation. The absorption system is used mainly in household units, but finds economical industrial application where cheap exhaust steam is available.

An ammonia refrigeration plant is a typical illustration of the vapor-compression system and is shown in Fig. 1.7. Table 1.8 gives properties of common refrigerating agents.

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Chapter 2

Coal Chemicals

Most chemicals from coal were initially obtained by destructive distillation, furnishing chiefly aromatics. In recent years, a substantial production of aromatics, particularly benzene, toluene, xylene, naphthalene, and methylnaphthalenes, has been obtained by processing petrochemicals (Chap. 38). With the advancing application of chemical conversion of coal, many more chemicals can be made from coal whenever it is economical to do so. Coal chemicals, however, except for metallurgical coke, are now in a very competitive field. Table 2.1 summarizes chemicals produced from coal as presented in this chapter and elsewhere in this book (see also Fig. 2.1 for many coal chemicals). Coal is the country's fundamental fuel, but petrochemicals now furnish most of the basic raw materials for many essential industries from dyes, medicines, pesticides, and elastomers to modern plastics. Coal forms the world's largest reserve of concentrated raw material[1] from which chemicals can be extracted and produced, and it also is a cheap source of heat and power used for processing. Although production of gas and aromatics from coal has been curtailed by petrochemical and natural gas competition, much new research and development is being conducted by U.S. government agencies and by private industry. In Chap. 3, on fuel gases, reference is made to the intense efforts to manufacture a fuel gas of high heating value and to supply demands for such gas. These efforts must also supply a substitute for natural gas as its supply diminishes. Other research is directed to making new or old chemicals from coal, lignite, and shale through improved technology and to continuing investigations with the aim of eventually supplying motor fuels and other organic chemicals from coal[2] at competitive prices.

THE DESTRUCTIVE DISTILLATION OF COAL[3]

When coal is thermally pyrolyzed or distilled by heating without contact with air, it is converted into a variety of solid, liquid, and gaseous products. The nature and amount of each

[1]OCR Calls for Petrochemicals from Coal, *Chem. Eng. News* 47 (1) 40 (1969).

[2]Process Utilizes Coal-derived Alkylphenols, *Chem. Eng. News.* 59 (48) 32 (1981); Perry, Coal Conversion Technology, *Chem. Eng.* 81 (15) 88 (1974); Spitz, Petrochemicals from Coal, *CHEMTECH* 7 (5) 297 (1977); Harris et. al., Chemicals from Coal, *CHEMTECH* 11 (12) 764 (1981).

[3]Lowry, *Chemistry of Coal Utilization,* Supplementary Volume, Wiley, New York, 1963 (121 references); Elliott. *Chemistry of Coal Utilization*, Second Supplementary Volume, Wiley-Interscience, New York, 1981 (encyclopedic); Berkowitz, *An Introduction to Coal Technology*, Academic, New York, 1979.

Table 2.1 Chemicals from Coal

	Chemical Conversion Process	Products and Procedures (numbers refer to chapters
a	Carbonization, pyrolysis of coal lignite, and carboniferous shales (destructive distillation)	Coal-tar aromatics, benzene and homologs, phenol and homologs naphthalene, anthracene phenanthrene, etc (5) High-temperature coke (5), low-temperature coke (5) Carbon for pigments (8), carbon for electrodes (5,8), structural material (8), activated carbon (8
b	Reduction and refining of ores	Iron, ferro alloys, etc., aluminum (14), magnesium (14)
c	Gasification (cf. *g* and *j*) Blue and producer gas are very minor	Coal gas (6), blue water gas (6), producer gas (6), peak gas (6), synthesis gas (6), CO_2 liquid and dry ice (7)
d	Combustion for comfort heating and power generation	Electric power utilities (4), comfort heating, retail deliveries (4), fly ash (4), sintered ashes for filters and concrete (4
e	Combustion for process heating	Heat for manufacture of lime (10), cement (10), ceramics (9), steel and rolling mills
f	Reduction, chemical	Sodium sulfite (11,12), sodium sulfide (12), barium sulfide (20), phosphorus (16)
g	Hydrogenation and hydrogenolysis, catalytic	Carbide process for aromatics (5), hydrogenation of coal Bergius process (5), Fischer-Tropsch liquid fuels (5,6), catalytic methanation of synthesis and pyrolysis gases (5,6)
h	Demethylation	Benzene from toluene or xylene (37), naphthalene from methylnaphthalenes (37)
i	Hydrolysis, alkaline	Mixed aromatics (5)
j	Oxidation, partial (controlled) and complete	Synthesis gas (7) for NH_3, CH_3OH etc., hydrogen (7), coal acids (5), carbon monoxide (7)
k	Electrothermal	Graphite (8) and electrodes (8), abrasives: silicon carbide (15), calcium carbide (15), cyanamide (18), carbon disulfide (15,38)
l	Sulfur recovery	H_2S from gas (6,7) Pyrite from coal
m	Sulfonation	Ion exchange, water softeners (3)
n	Solvent extraction of coal	Ashless coal, montan wax (28, humic acids, coumarone resins (34)

SOURCES: Lowry, *Chemistry of Coal Utilization*, vols 1 and 2, Wiley, New York, 1945, suppl. vol., 1963; Future for Fossils, *Chem. Week* 115 (15) 46 (1974). Perry, op cit (several flowcharts); Iammartino, *Chem. Eng.* 81 (21) 68 (1974); McMath et al. Coal Processing; A Pyrolysis Reaction for Coal Gasification, *Chem. Eng. Prog.* 70 (6) 72 (1974); Chemical Communication Shows Promise for Coal, *Chem. Eng. News* 52 (35) 16 (1974); UOP Set to Scale Up Oil-from-Coal Process, *Chem. Eng. News* 52 (38) 7 (1974).

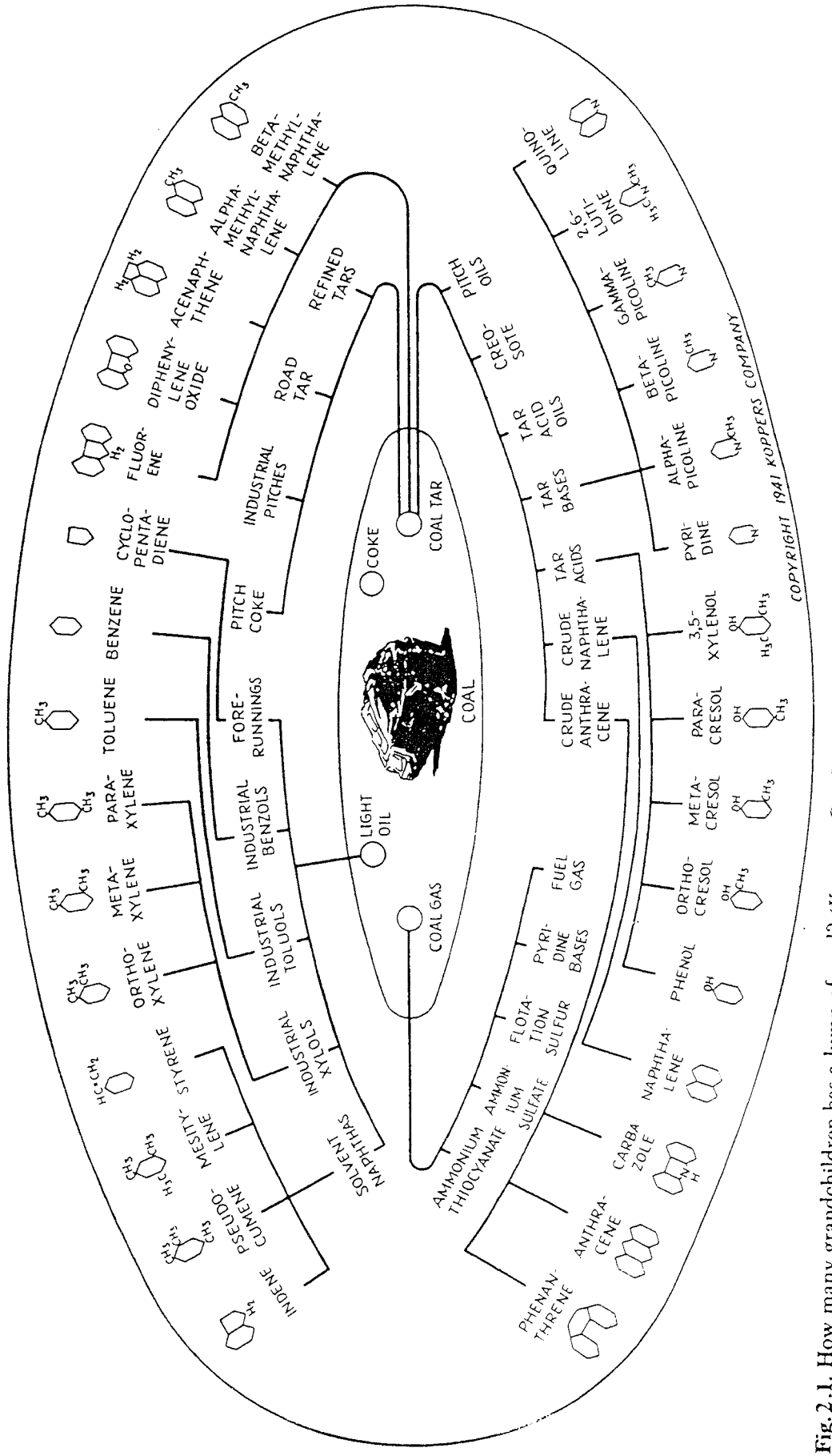


Fig. 2.1. How many grandchildren has a lump of coal? *(Koppers Co., Inc.)*

product depends upon the temperature used in the pyrolysis and the variety of the coal used. In ordinary practice, coke-oven temperatures are maintained above 900°C but may range anywhere from 500 to 1000°C. The principal product by weight is coke. If a plant uses temperatures from 450 to 700°C, the process is termed *low-temperature carbonization*; with temperatures above 900°C it is designated *high-temperature carbonization*. In low-temperature carbonization the quantity of gaseous products is small and that of the liquid products is relatively large, whereas in high-temperature carbonization the yield of gaseous products is larger than the yield of liquid products, the production of tar being relatively low.

Low-temperature carbonization produces liquids strikingly different from those produced by high-temperature carbonization, even when using the same coal. Low-temperature liquids contain more tar-acids and tar-bases than high-temperature liquids. The market for low-temperature liquids is not yet well-established. With high-temperature carbonization, the liquid products are water, tar, and crude light oil. The gaseous products are hydrogen, methane, ethylene, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia, and nitrogen. The products other than coke are collectively known as coal chemicals, or *by-products*.

The destructive distillation of coal, or its carbonization, is really a striking example of chemical conversion, or the process of pyrolysis. This chapter outlines the equipment needed to carry out, on a commercial scale, the basic chemical changes that take place. The chemical theory of the pyrolysis of coal[4] indicates the following step-by-step decomposition.

1. As the temperature is raised, the aliphatic carbon-carbon bonds break first. Reaction begins below 200°C.
2. Carbon-hydrogen linkages break next at or near 600°C.
3. The elimination of heterocycle complexes and progressive aromatization are the essential reactions taking place during the decomposition as the carbonization proceeds.
4. The molecular weights of the intermediate products regularly decrease as the temperature rises. Water, carbon monoxide, hydrogen, methane, and other hydrocarbons are evolved.
5. Decomposition is at a maximum between 600 and 800°C. All the above reactions vary markedly in their extent depending on the rate of heating as well as the temperature attained.

Hill and Lyon[5] suggest that "coal consists of large heterocyclic nuclei-monomers, with alkyl side chains held together by three-dimensional C—C groups, and includes functional oxygen groups." (See Fig. 5.2.)

HISTORICAL. It is known that coke was an article of commerce among the Chinese over 2000 years ago, and in the Middle Ages it was used in the arts for domestic purposes. Nevertheless, it was not until 1620 that the production of coke in an oven was first recorded. Up until the middle of the nineteenth century, coal tar and coal-tar products were regarded as waste. Synthesis of the first coal-tar color, by Sir William Perkin in 1856, caused a great demand for coal tar, and it became a commercial product of increasing value. Perkin, with his discovery of the brilliant violet dye, mauve (Chap. 39), while attempting the synthesis of quinine through the oxidation of crude aniline in England, laid the foundation of the world's coal-tar-dye industry. In 1792, the first successful experiment involving the production of gas

[4]Fuchs and Sandhoff, Theory of Coal Pyrolysis, *Ind. Eng. Chem.* 34 (5) 567 (1942). Lowry, op. cit., p. 379.

[5]Hill and Lyon, A New Chemical Structure for Coal, *Ind. Eng. Chem.* 54 (6) 37 (1962). Elliott, op. cit.

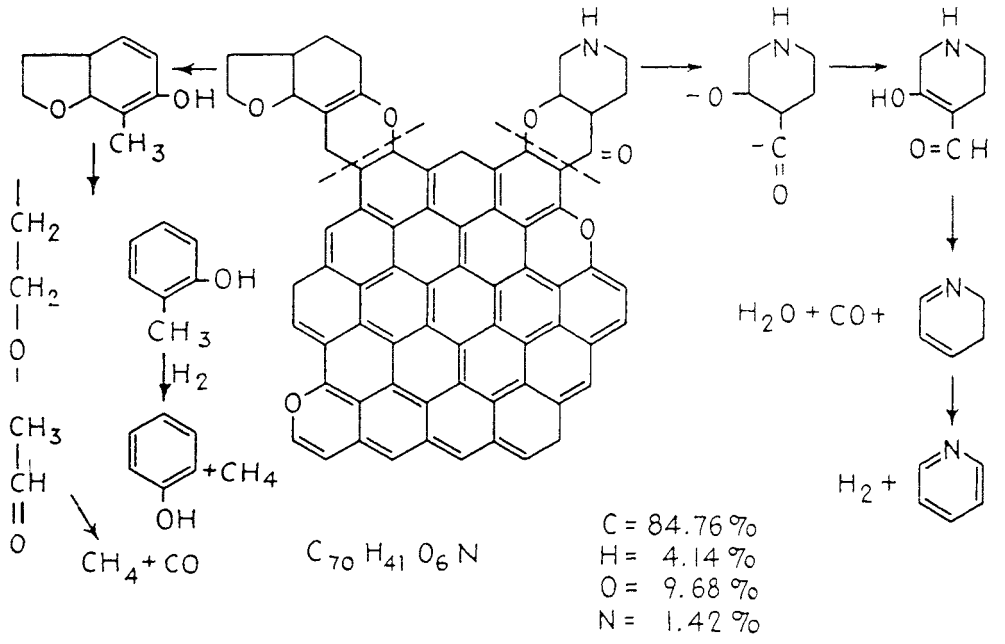


Fig. 2.2. Example of coal pyrolysis. *(After Fuchs and Sandhoff)*

from coal was carried out by William Murdock, who made it possible to light the streets of London with gas in 1812. The first battery of Semet-Solvay ovens was erected in Syracuse, N.Y. in 1893.

USES AND ECONOMICS. Coke is the product of largest tonnage from the distillation of coal. The demand for coke depends on the demand for steel. About 98 percent of coal-tar production is from by-product ovens.[6] See Table 2.2 for data on crude aromatics from coal and petroleum. Until recent years aromatic crudes and the pure compounds derived therefrom were based exclusively on coal tar. Now that the petroleum industry supplies so many aromatics, the chief incentive in distilling coal is to supply coke for steel. The liquid products, comprising coal-tar and ammonia liquor, are not so large in volume as the solid products of coal distillation, but they are of importance to chemical-recovery ovens. A considerable volume of coal tar is still used as fuel, and for roofing and roads. Aromatics from petroleum and coal tar are made into dyes, intermediates, medicinals, flavors, perfumes, resins, rubber chemicals, and thousands of other useful products that are almost indispensable to our present civilization.

COKING OF COAL

Although coke can also be made from petroleum (see Heavy Distillates, Chap. 37), the two main types of coking procedures for coal were the beehive and the by-product. Beehive coking is the obsolete, primitive method. In by-product ovens the carefully blended coal charge is heated on both sides so that heat travels toward the center and thus produces shorter and more solid pieces of coke than are made in the beehive oven. Air is excluded so that no burning takes place within the oven, the heat being supplied completely from the flues on

***Table* 2.2** U.S. Production of Tar and Tar Crudes (in millions of liters except where noted otherwise)

Product	Production				
	1953	1964	1972	1979	1980
Crude light oil	1151	941	811	398	602
Intermediate light oil	4.0	20.4	14.0	n.a.*	n.a.
Light oil distillates					
Benzene, specification and industrial grades, total	919	2764	4741	6332	7585
Tar distillers	122	—	—	—	—
Coke-oven operators	672	450	302	231	192
Petroleum operators	239	2314	4439	6101	7396
Toluene, all grades, total	591	1874	3467	3823	3845
Tar distillers	17.7	—	—	—	—
Coke-oven operators	136	96.2	55.2	35.0	29.5
Petroleum operators	437	1777	3412	3788	3816
Xylene, total	430	1299	2798	3680	3434
Coke-oven operators	37.6	26.9	12.7	5.2	5.1
Petroleum operators	389	1272	2786	3675	3429
Solvent naphtha, total	59.3	—	—	—	—
Tar distillers	35.5	—	—	—	—
Coke-oven operators	23.0	17.0	10.7	5.1	—
Other light oil distillates, total	55.5	—	—	—	—
Tar distillers	32.4	—	—	—	—
Coke-oven operators	23.1	34.5	26.1	—	—
Pyridine crude bases, dry basis	2.09	1.76	—	—	—
Naphthalene, crude	125	193	186	—	—
Crude tar-acid oils	—	105	36.8	72.0	61.6
Creosote oil, dead oil	550	429	527	408	229
All other distillate products	70	—	—	—	—
Tar, road	416	211	113	—	—
Tar, miscellaneous uses, t	138	75.6	54.5	51.6	45.3
Pitch tar, t	1712	1706	1244	n.a.	1083
Hard tar, t	645	901	715	—	—

*n.a., not applicable

†Where dashes occur, data are not available, usually because publication would disclose individual producer data. This is prohibited by law.

SOURCE: *Synthetic Organic Chemicals*, International Tariff Commission, 1953–1980.

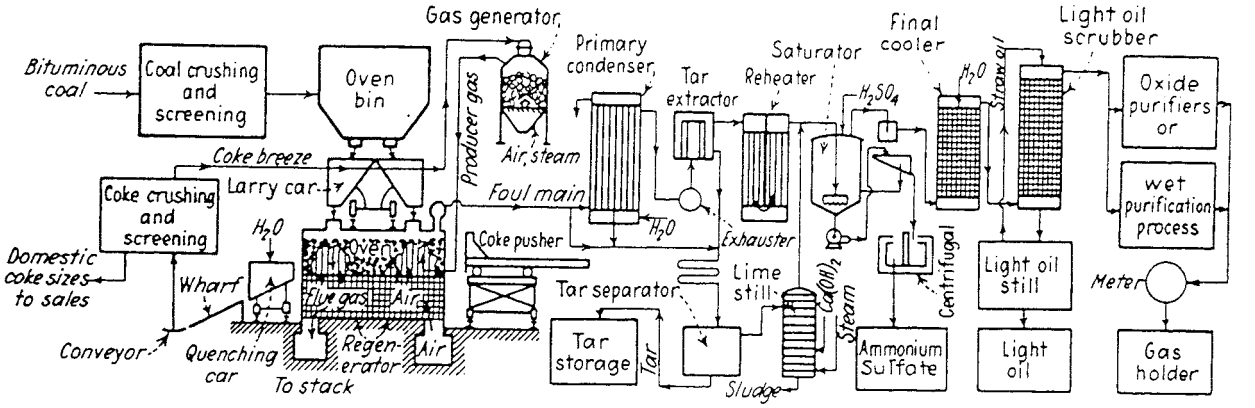
the sides. About 40 percent of the oven gas, after being stripped of its by-products, is returned and burned for the underfiring of the battery of ovens, and some is used for fuel gas locally.

Beehive coking disappeared from the United States because it was a small batch process and produced a very large amount of pollution. It continues to be used in many places abroad.

BY-PRODUCT COKING. The by-product coke oven is a narrow chamber, usually about 11 to 12 m long, 4 m high, and tapering in width from 0.4 to 0.6 m at one end to 0.35 to 0.4 m at the other. The ovens hold from 15 to 25 t of coal.[6a] These ovens are used for carbonizing coal only in large amounts and are built in batteries of 10 to 100 ovens. The general arrangement for the operation of a by-product coke oven with its various accessories, followed by the initial treatment of its by-products, is depicted[7] in Fig. 5.3.

[6a] t = 1000 kg

[7] Lowry, op. cit., chap. 11, p. 461 (121 references) and Elliott, op. cit.



In order to produce: 0.28–0.35 Mm^3 of 20.5 MJ/m^3 gas; 700 kg coke; 38 L tar; 11.4 kg ammonium sulfate; 7.6–15.2 L light oil, the following materials are required.

Bituminous coal	1 t	Steam	200–600 kg
Sulfuric acid (60°Bé)	12.5 kg	Electricity	25 MJ
Lime	0.75–1 kg	Direct labor	0.8–1.3 work-h
Water	4150–8000 L		

Fig. 2.3. By-product coke-oven procedures.

The by-product coke oven is one of the most elaborate and costly of masonry structures and is erected with the closest attention to engineering details, so that it can withstand the severe strains incurred in its use and remain gastight even after the great expansion caused by the heating up. The oven block is built of refractory brick, with heating flues between the coking ovens, as shown in Fig. 2.4.

The individual by-product coke oven operates intermittently, but each oven is started and stopped at different times, so that the operation of the entire block continually produces gas of good average composition. A charge of finely crushed coal is dropped from a larry car through charging holes (usually four, though the generalized flowchart of Fig. 5.3 shows only two) in the top and into the oven, where the walls are at approximately 1100°C. The surface of the coal in the oven is leveled and the charging holes are then covered. Heating is carried out and the charge left in the oven until it is completely coked and the evolution of volatile matter has ceased. The average temperature at the center of the charge at the end of the heating period is usually about 980°C, and the average flue temperature is about 1290°C. Temperatures vary with the conditions of operation, the coking time, the width of the oven, and the type of coal, its moisture content, and its fineness of division. By-product ovens are no longer operated to make a large volume of high-grade coal tar or gas but to make the best quality furnace coke for steel mills. At the end of the coking time (approximately 17 h) the doors at the end of the oven are opened and the entire red-hot mass is pushed out through the oven from end to end in less than a minute by an electrically driven ram. The coke falls into a quenching car, which holds the charge from one oven. The coke is quenched with water, thus cooling it and preventing it from catching on fire. In the U.S.S.R. and Japan some plants use a "dry quenching" system, which recovers some of the sensible heat.

The gas from the destructive distillation of the coal, together with entrained liquid particles, passes upward through a cast-iron gooseneck into a horizontal steel pipe, which is connected to all the ovens in a series. This pipe is known as the collecting main and is sometimes called a hydraulic main. As the gas leaves the ovens, it is sprayed with weak ammonia water. This condenses some of the tar and ammonia from the gas into liquid. The liquids move

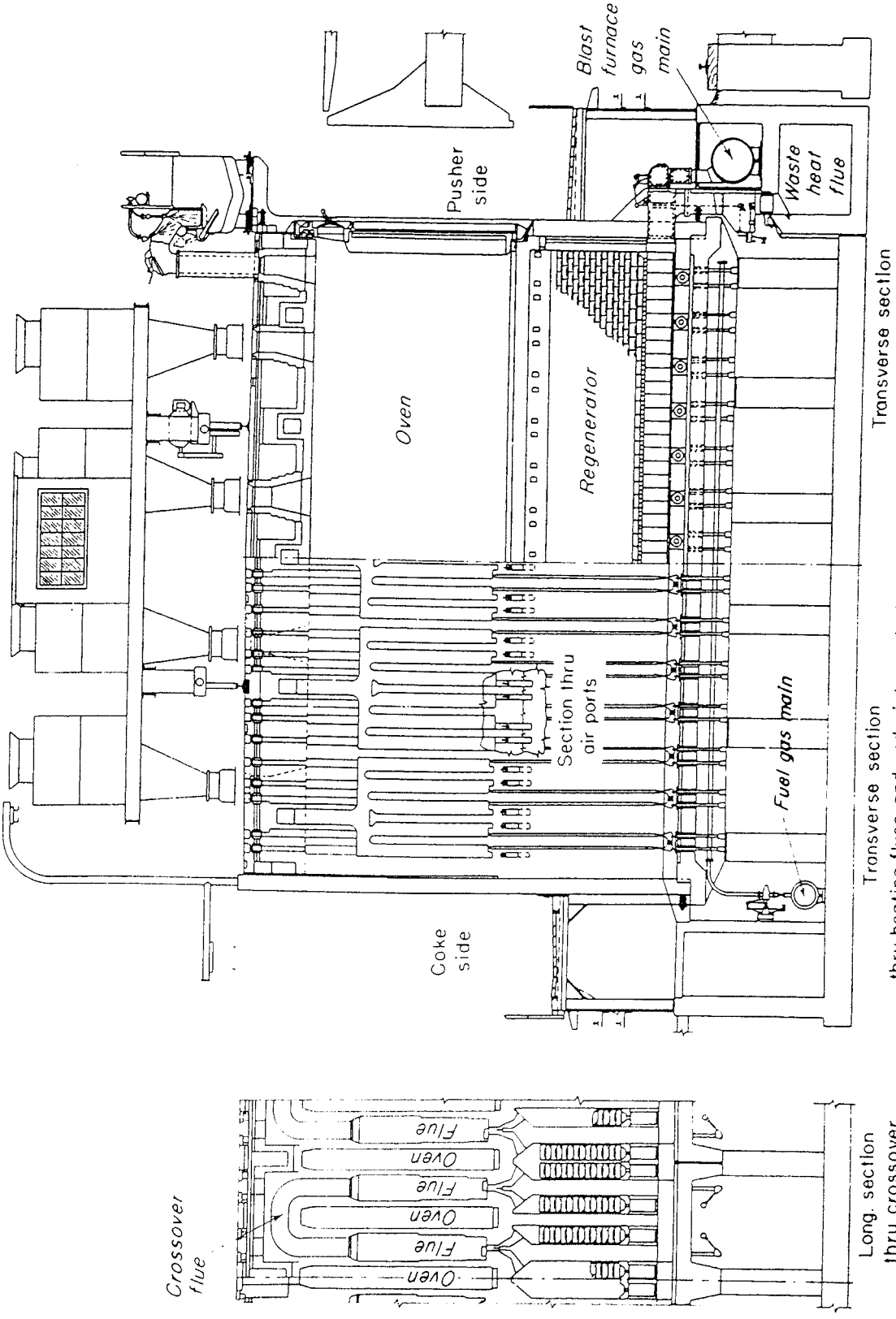


Fig. 2.4. Koppers-Becker underjet low-differential combination coke oven with waste-gas recirculation. (*Koppers Co., Inc.*)

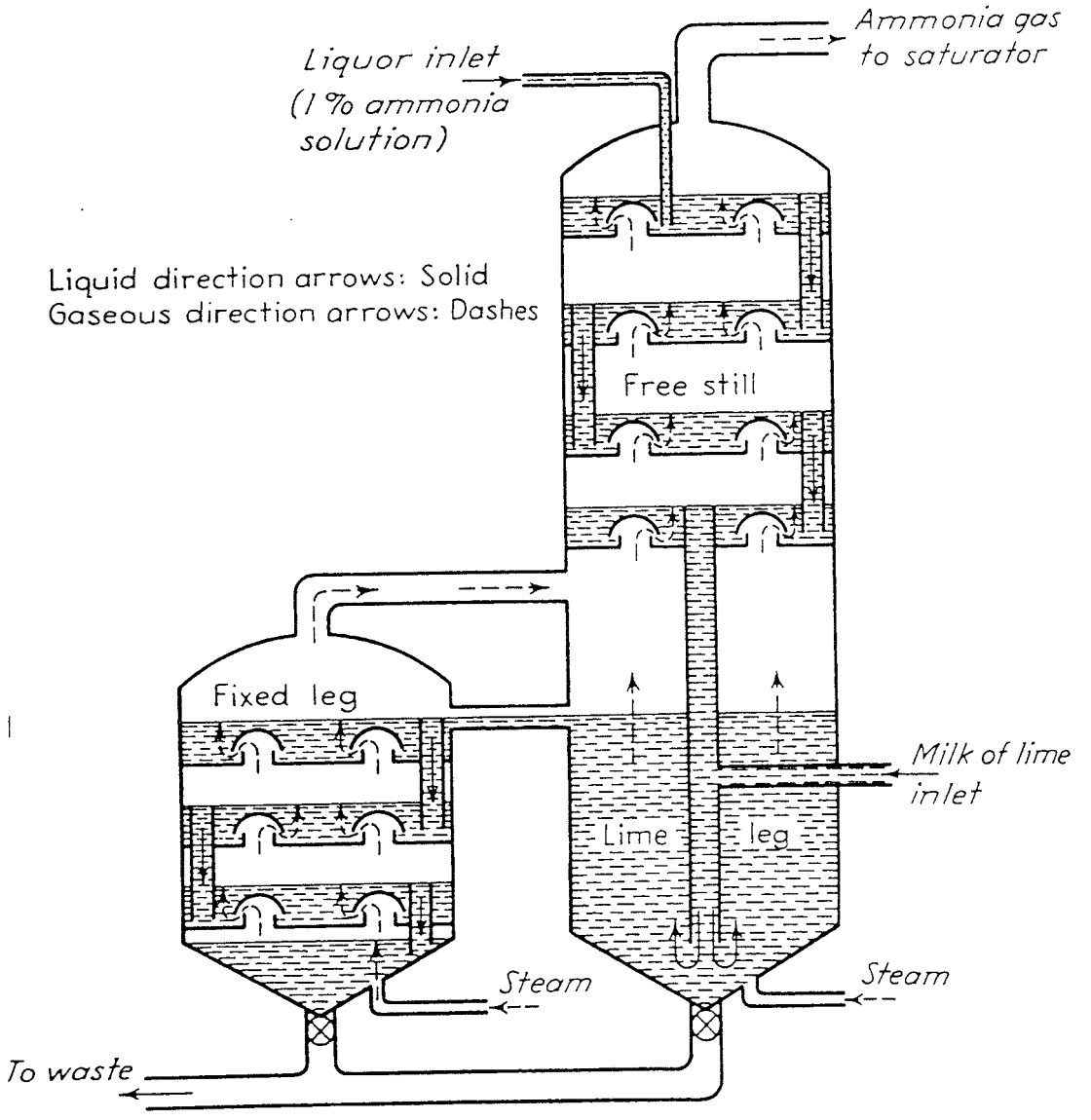


Fig. 2.5. Diagram of an ammonia still. It operates with a drain from the fixed leg opened sufficiently to prevent accumulation of liquor in this section. The drain from the lime leg is closed except for cleaning.

through the main along with the gases until a settling tank is reached, where separation is effected according to density. Some of the ammonia liquor is pumped back into the pipes to help condensation; the rest goes to the ammonia still (Fig. 2.5), which releases the ammonia for subsequent chemical combination in the saturator. All the tar flows to storage tanks for tar distillers or for fuel.[8]

Figure 2.3 can be divided into different steps, representing the flow of material through the various pieces of equipment, wherein the proper physical operation or chemical conversion takes place. Figure 2.3 may be thus broken down into the following sequences:

Coal is transferred, crushed, and screened.
Coal is charged to a hot, empty oven.
Coal is chemically transformed to coke and volatiles by pyrolysis.
Hot coke is pushed out of the oven, quenched, and transported.

[8]Lowry, op. cit., p. 462, for other types of ovens.

Condensable products of distillation are liquefied and collected in the hydraulic main.
Foul gas is cooled, and tar extracted.
Ammonia is removed from gas as ammonium sulfate.
Gas is cooled and subjected to benzene and toluene removal by absorption in straw oil.
Hydrogen sulfide is removed.
Purified gas is metered and transferred to consumers.

The tar separated from the collecting main and the tar extractors or electrostatic precipitators is settled from ammonia liquor and, together with light oil, subjected to the sequences represented by the flowchart (Fig. 2.6). The pipe still is of the radiant-heated type. The crude tar feed inlet can be seen at the lower right. The tar is filtered and pumped through the reflux vapor-tar heat exchanger, economizer, pitch-tar heat exchanger into the top of the lower third of the distillation column and out at the bottom, to the circulating pumps and into the pipe still (where the crude tar joins 4 to 5 volumes of the circulating pitch and on finally to near the top of the distillation column). The vapors, steam distilled and superheated, pass overhead from the top of the tray-type distillation column, enter the bottom of the bubble-cap fractionating column, and are separated into four fractions 1, 2, 3, 4, with a residue 5, leaving at the bottom of this fractionating column. The product pitch, 6, cascades from the top of the distillation column down through the superheated steaming section to establish the desired pitch hardness and to strip this pitch of the higher-boiling volatile oils. It is then withdrawn from above the middle of the distillation column and conducted through the pitch-tar heat exchanger to storage. The products are:

	Product	Boiling Point, °C
Side stream 1	Light oil	to 170
Side stream 2	Carbolic oil	170–205
Side stream 3	Naphthalene oil	205–240
Side stream 4	Creosote or wash oil	240–280
Residue 5	The residue or anthracene	270–340
Pitch 6	Residuum or pitch	325–400

There are standby steam pumps in the event of failure of the motor-driven pumps. The Wilton principle of recirculation of hot pitch at 350°C, mixed with the crude tar at 120°C, raises the temperature of the pitch-tar leaving the pipe still to only 350°C and avoids thermal cracking and vaporization in the pipe still.

Koppers-Becker ovens are the most widely used vertical-flue ovens in the United States. The elevation is shown in Fig. 2.4. These ovens are all of the regenerative type and have individual heat regenerators, generally from side to side, underneath the oven. The gas burns upward, crosses over the top of the oven, comes downward on the other side, and exits through the regenerator oven underneath. The reversal of the air and waste gas flow is made from side to side every half hour.

Coke and char can be made by continuous processes, but the liquid products and the coke formed vary greatly from the products obtained from a by-product oven.

Low-temperature carbonization once looked promising as a method of producing fuel gas and reactive char, which is useful as a smokeless fuel for domestic heating. Several continuous processes, for example, the Lurgi-Spulgas retort, have had some success in Europe. In the

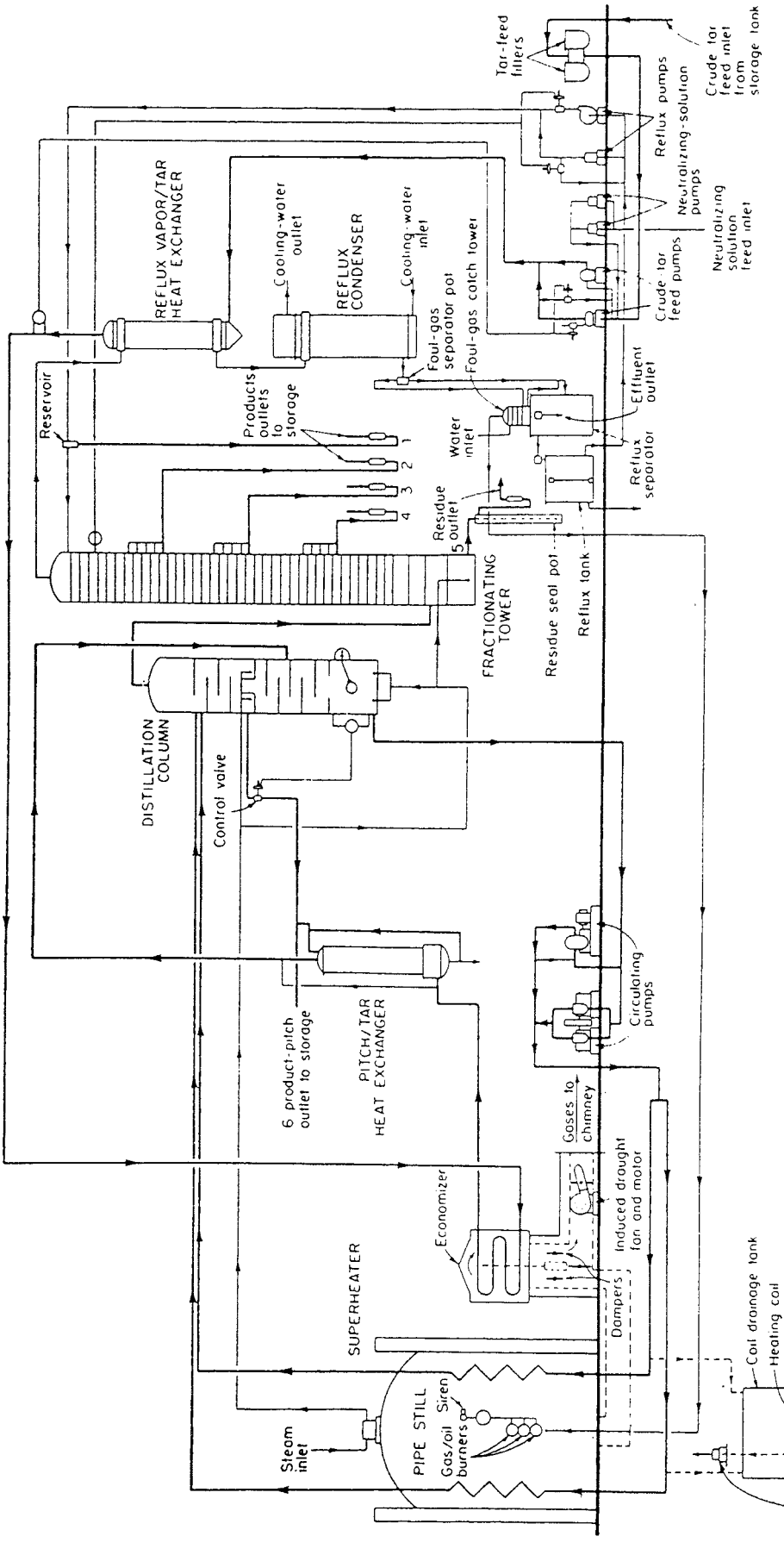


Fig. 2.6. Flowchart of coal-tar continuous distillation (without tar dehydration). *(Chemical Engineering, Wiltons Ltd., London. See special pamphlets from this company for details.)*

United States, a strong demand for low-temperature liquids has never developed, and the char has not become a popular home fuel, so these processes have not prospered.

High-temperature continuous carbonizers are usually operated to produce synthesis gas with low yields of coke (see Chap. 6). It is possible to produce finely divided high-temperature coke with synthesis-gas reactors, and then to compact the product to form metallurgical coke briquettes (formcoke) for blast furnaces, but this is apparently not currently profitable

RECOVERY OF COAL CHEMICALS.[9] The gaseous mixture leaving the oven is made up of permanent gases that form the final purified coke-oven coal gas for fuel, along with condensable water vapor, tar, and light oils, and solid particles of coal dust, heavy hydrocarbons, and complex carbon compounds. Significant products recoverable from the vapors include: benzene, toluene, xylenes, creosote oils, cresols, cresylic acid, naphthalene, phenols, xylols, pyridine, quinoline, and medium and hard pitches usable for electrode binders, road tar, or roofing pitch. Many others exist in appreciable quantity and await the finding of suitable uses to make their recovery economically possible. The gas is passed from the foul main (Fig. 2.3) into the primary condenser and cooler at a temperature of about 75°C. Here the gases are cooled by water to 30°C. The gas is conducted to an exhauster, which serves to compress it. During the compression the temperature of the gas rises as high as 50°C. The gas is passed to a final tar extractor, where the tar is thrown out by impingement against metal surfaces. In newer plants the tar extractor may be replaced by electrostatic precipitators. On leaving the tar extractor, the gas carries three-fourths of the ammonia and 95 percent of the light oil originally present when it left the oven.

The gas is led to a saturator (Fig. 2.3) containing a solution of 5 to 10% sulfuric acid[10] where the ammonia is absorbed, and crystalline ammonium sulfate is formed. The gas is fed into the saturator, a lead-lined or stainless-steel closed vessel, through a serrated distributor underneath the surface of the acid liquid. The acid concentration is maintained by the addition of 60°Bé sulfuric acid and the temperature is kept at 60°C by the reheater and the heat of neutralization. The crystallized ammonium sulfate is removed from the bottom of the saturator by a compressed-air ejector, or a centrifugal pump, and drained on a table, from which the mother liquor is run back into the saturator. The salt is dried in a centrifuge, and bagged, usually in 50-kg sacks (Chap. 18).

The gas leaving the saturator is at about 60°C; it is taken to final coolers or condensers, where it is scrubbed with water until its temperature is 25°C. During this cooling, some naphthalene separates and is carried along with the wastewater and recovered. The gas is passed into a light oil or benzol scrubber (Fig. 2.3), through which the absorbent medium, a heavy fraction of petroleum known as straw oil, or sometimes a coal-tar oil, is circulated at 25°C. The straw oil is sprayed into the top of the absorption tower while the gas flows upward through the tower. Most scrubbers use some form of metal packing to increase the contacting surface area, although wooden grids were formerly used. The straw oil is allowed to absorb about 2 to 3 percent of its weight of light oil, with a removal efficiency of about 95 percent of the light oil vapor in the gas.

The rich straw oil, after being warmed in heat exchangers by vapors from the light-oil still and then by hot debenzolized oil flowing out of the still, is passed to the stripping column

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[9]Details of this recovery of the many coal chemicals are to be found in Lowry, op. cit., p. 618; for tar processing and light oil processing see ECT, 3d ed., 1982.

[10]At the start of a charge the acid concentration is often as high as 25%, but ammonium bisulfate is liable to be formed when free sulfuric acid exceeds 10 to 11%.

Table 2.3 Approximate Yields per Metric Ton of Coal Carbonized
(Depending on Coal and Conditions Used)

	High-Temperature, kg	Low-Temperature, kg
Furnace coke	715	—
Coke breeze	46.5	—
Semicoke (12% volatiles)	—	720
Tar	39	75
Ammonium sulfate*	10	9
Light oil (removed from gas by oil scrubbing; see Table 5.4)	10	8
Gas	1750	125

*Note that 4 kg of technical ammonium sulfate is equivalent to 1 kg of ammonia.
SOURCE: *Ind. Eng. Chem.* 48 352 (1956). See also Fig. 2.3.

where the straw oil, flowing downward, is brought into direct contact with live steam. The vapors of the light oil and steam pass off and upward from the still through the heat exchanger previously mentioned and into a condenser and water separator. The lean, or stripped, straw oil is returned through the heat exchanger to the scrubbers. The gas, after having been stripped of its ammonia and light oil, has the sulfur removed in purifying boxes, which contain iron oxide on wood shavings, or by a solution of ethanolamine (Girbotol) in scrubbing towers, the best present-day practice. These procedures are fully described in Chaps. 3 and 4.

An alternate procedure[11] uses ammonium phosphates to absorb the ammonia. $NH_4H_2PO_4$ absorbs ammonia to form more alkaline phosphates such as $(NH_4)_2HPO_4$ and $(NH_4)_3PO_4$, which are returned to the original form by steaming, thus releasing the ammonia. This is the Phosam process. In a typical absorption cycle, lean 40% phosphate solution (the molar ratio of NH_3/H_3PO_4 is less than 1.5) soaks up all but traces of NH_3. The rich ammonium phosphate solution is reboiled in a distillation tower in which NH_3 vapor and a lean phosphate solution are separated for reuse.

LOW-TEMPERATURE CARBONIZATION.[12] In this century a large amount of experimental work has been carried out on the carbonization of coal at temperatures ranging from 400 to 600°C with the main object of obtaining maximum yields of liquid products and producing semicokes (chars) containing 8 to 20% volatile matter. Here again the characteristics and yields of the various products depend upon the coal, the temperature, and the treatment. Tables 2.3 and 2.4 show the difference in gas content and in yield products for high- and low-temperature systems. The Disco plant at McDonald, Pa., utilizes a low-temperature carbonization process[13] and has a daily capacity to convert high volatile coal into 800 t of Disco Char, a domestic fuel. The tar is sold and refined to tar-acid oil, tar acids, "creosote,"[14] and fuel pitch. The gas, after liquid products removal, is used for firing the ovens. The maximum temperature used in this process is 570°C.

[11]U.S. Patent 3,024,090.

[12]Lowry, op. cit., chap. 10, p. 395 (138 references).

[13]Lowry, op. cit., p. 439.

[14]By definition of the American Wood Preservers Association, however, creosote is a distillate of high-temperature coke-oven tar.

Table 2.4 Variation of Gas from Low- and High-Temperature Coal Carbonization

Gas	Coking Temperature 500°C, %	Coking Temperature 1000°C, %
CO_2	9.0	2.5
C_nH_m	8.0	3.5
CO	5.5	8.0
H_2	10.0	50.0
CH_4 and homologs	65.0	34.0
N_2	2.5	2.0

DISTILLATION OF COAL TAR

Coal tar is a mixture of many chemical compounds, mostly aromatic, which vary widely in composition (Figs. 2.2 and 2.7). It is a by-product of the destructive distillation or pyrolysis of coal. Most of the tar in this country is produced as a by-product of the manufacture of blast-furnace coke. The quality and quantity of tar from this operation will vary, depending on the rate of production of the ovens and the nature of the coal used. The specific gravity will vary from 1.15 to 1.2, and the quantity of tar will vary from 30 to 45 L of tar per metric ton of coal. A typical light-tar composition is shown in Fig. 2.7. The end product of the distillation (Fig. 2.6) of coal tar is pitch, usually more than 60% of the crude tar. The object of the distillation is to produce a salable end product, with a separation of the valuable products into useful cuts. In a modern refinery equipped with a fractionating column (Figs 2.6 and 2.8) for the primary distillation, these products must usually be sharply fractionated, with a minimum of overlapping. The process must also be thermally economical, and the furnace (Figs. 2.6 and 2.9) so designed and constructed that repairs and fuel usage are at a minimum. No one product exceeds 0.5% of the crude.

METHODS OF DISTILLATION. There have been many improvements in coal-tar distillation over the years. These can be divided into three general classifications:

1. The 10,000- to 30,000-L batch still (obsolete, but a few are still being operated), which has been much improved and used for special end products such as pipe enamel (Fig. 2.9).
2. The continuous still, with a single distillation column, using side-streams (Fig. 2.9).
3. The continuous unit, using multiple columns with reboilers (Fig. 2.8). Recirculation of the residue improves the operation.

The use of techniques derived by the petroleum industry has reduced costs and greatly improved product purities.

PRODUCTS OF DISTILLATION. Modern practice, as exemplified by the pipe still and fractionating columns, is producing such clean-cut fractions that further purification is rarely required. Figure 2.6 shows the fractions obtained in an ordinary distillation, which will vary with the coal tar and the conditions.

1. Light oils usually comprise the cut up to 200°C. They are first crudely fractionated and agitated at a low temperature with concentrated sulfuric acid, neutralized with caustic soda, and redistilled, furnishing benzene, toluene, and homologs (Table 2.5).

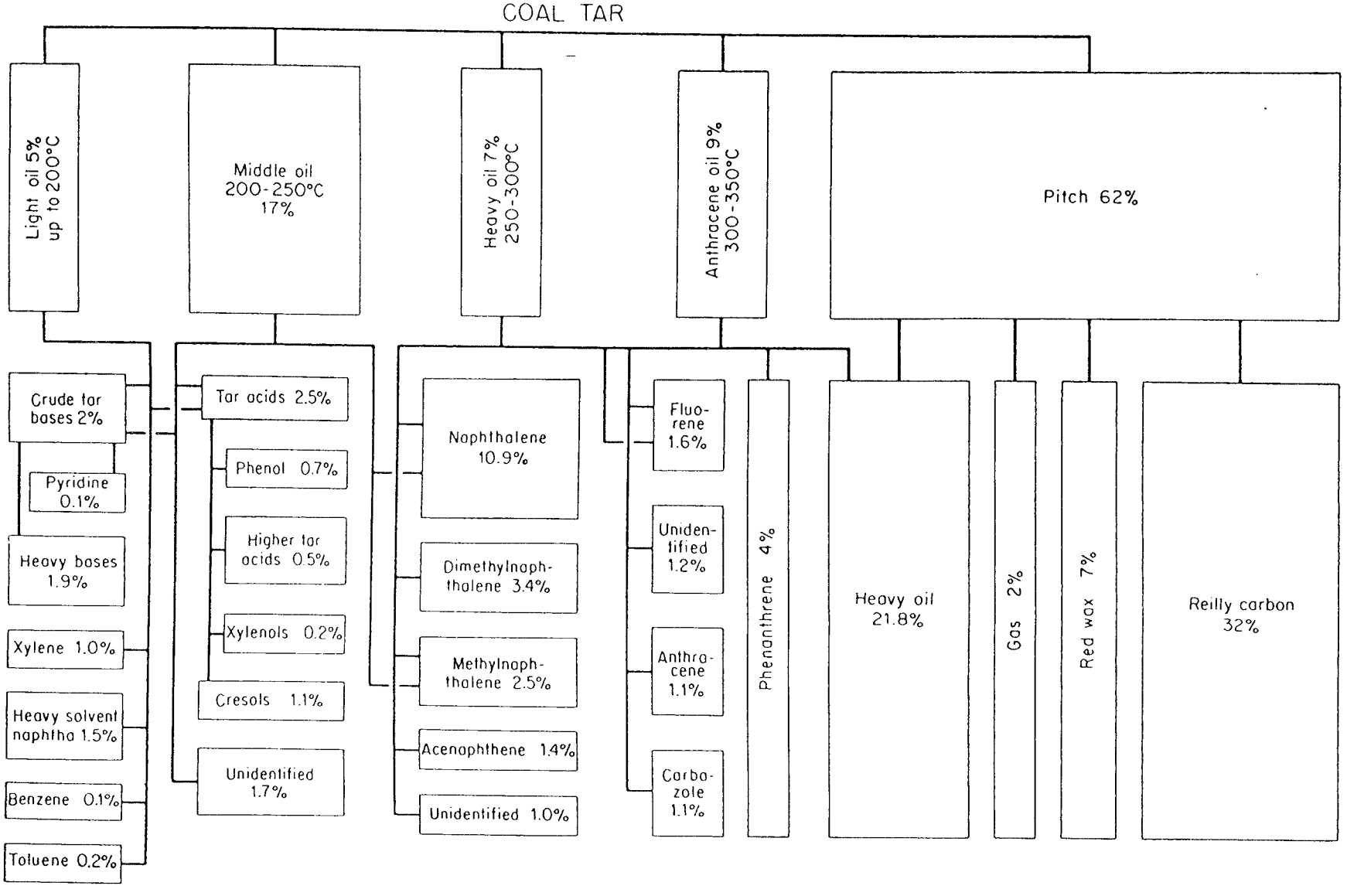

Fig. 2.7. Principal products from coal tar. The crude coal-tar distillates as obtained in practice and the products derived therefrom. The percentage yields as shown and represented by the area of the rectangles are *average values* based on the original tar. Yields vary with different conditions and different coals. Another coal tar of 1.1 to 1.2 sp gr analyzed as follows: benzol and toluol (crude benzene and toluene) 1.0%, other light oils 0.7%, phenol 0.3%, cresols 0.3%, naphthalene 4.3%, creosote oil 28.3%, anthracene 0.3%, and pitch 64.8%. *(Reilly Tar and Chemical Corp.)*

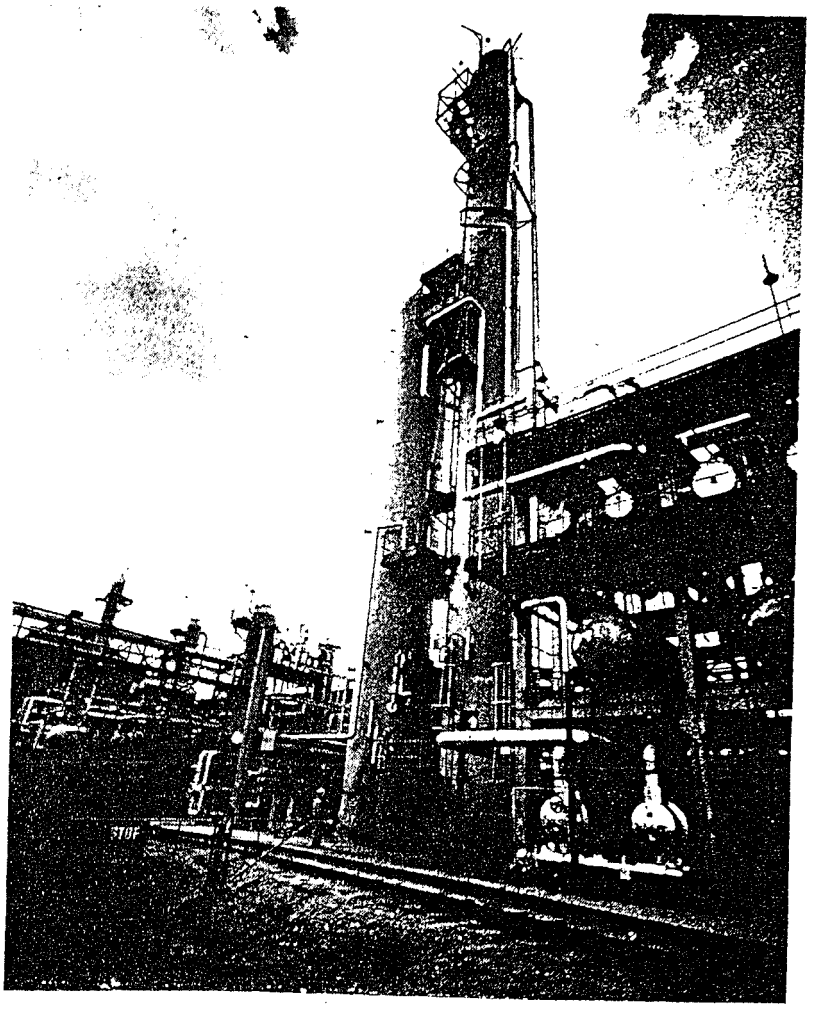

Fig. 2.8. Fractionating distilling column (height 45 m) at Clairton, Penn., producing high-quality benzene, toluene, and xylenes. *(U.S. Steel Co.)*

2. Middle oils, or creosote oils, generally are the fraction from 200 to 250°C, which contain naphthalene, phenol, and cresols. The naphthalene settles out on cooling, is separated by centrifuging, and is purified by sublimation. After the naphthalene is removed, phenol and other tar acids[15] are obtained by extraction with 10% caustic soda solution and neutralization, or "springing" by carbon dioxide. These are fractionally distilled.

3. Heavy oil may represent the fraction from 250 to 300°C, or it may be split between the middle oil and the anthracene oil.

4. Anthracene oil is usually the fraction from 300 to 350°C. It is washed with various solvents to remove phenanthrene and carbazole; the remaining solid is anthracene.

MISCELLANEOUS USES OF COAL TAR. A substantial fraction of the coal tar produced continues to be used as fuel. Coal tar is also utilized for roads and roofs. For these purposes the tar is distilled up to the point where thermal decomposition starts. This "base tar" is then oiled back (diluted) with creosote oil to ensure satisfactory rapid drying. Similar tars are used to impregnate felt and paper for waterproofing materials.

[15]"Tar acids," in the language of the tar distiller, represent phenol and homologs, which are soluble in caustic soda.

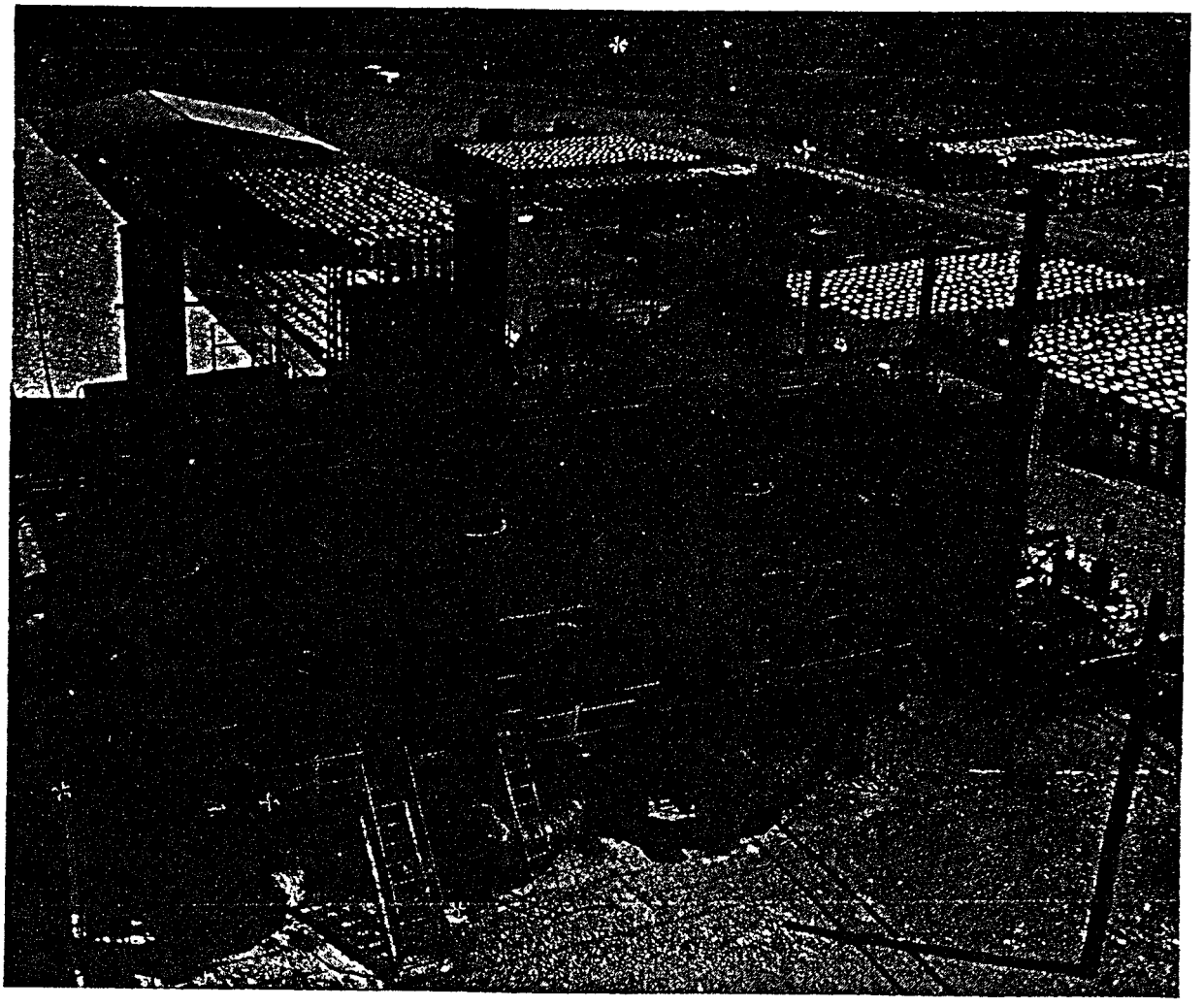

Fig. 2.9. Stirred batch tar-distillation stills. *(Reilly Tar and Chemical Co.)*

FRACTIONATION AND PURIFICATION OF COAL-TAR CHEMICALS. Largely because of the present competition from aromatic chemicals produced from petroleum (Chap. 38), interest in aromatics from coal has temporarily decreased (see Table 2.2 for main products). At one time coal tar was the sole source of pyridine; however synthetic processes using aldehyde and ammonia are now supplying the increased demand. This is also true of phenol (Chap. 34). In

Table 2.5 Typical Composition of Light Oil from Gas*

	kg/t
Benzene	15.2
Toluene	3.6
Xylenes and light solvent naphtha	2.4
Acid washing loss (mainly unsaturateds)	1.3
Heavy hydrocarbons and naphthalene	2.2
Wash oil	1.8
Total crude light oil	26.5
Pure motor fraction	20.6

*Calculated from Lowry, op. cit.

***Table* 2.6** Some Important Constituents of European Coal Tar

Compound	%	Compound	%
Naphthalene	10	Diphenyl	0.4
Phenanthrene	5	Indole	0.2
Fluoranthene	3.3	2-Phenylnaphthalene	0.3
Pyrene	2.1	Isoquinoline	0.2
Fluorene	2.0	Quinaldine	0.2
Chrysene	2.0	Acridine	0.6
Anthracene	1.8	Phenanthridine	0.2
Carbazole	1.5	7,8-Benzoquinoline	0.2
2-Methylnaphthalene	1.4	Thianaphthene	0.3
Dibenzofuran	1.0	Diphenylene sulfide	0.3
1-Methylnaphthalene	1.0		

SOURCE: *Ind. Eng. Chem.* 55 (5) 38 (1963).

Europe,[16] which has much coal and little petroleum, there is continued interest in coal chemicals. Table 2.6 lists some solid chemicals that *could* be obtained from coal tar. The product of largest potential is phenanthrene (the second most abundant material in coal tar), of which Franck estimates that 250,000 t can be recovered in the western world yearly as soon as profitable uses can be found. This is based on a total recovery of 10^7 t of crude tar with a 50 percent yield. Anthraquinone (Chap. 39) is the basis of many vat dyes, but it is cheaper to synthesize it (Chap. 39) from phthalic anhydride than to oxidize anthracene.

COAL TO CHEMICALS

This section considers the rest of the processes listed in Table 2.1, except those designated for discussion in other chapters. In all cases other details are available in the references, especially in the volumes edited by Lowry and Elliott.

Solvent extraction of coals and lignites has been tried at temperatures below and above 300°C and with and without mild hydrogenation. Simple extraction of coal at low temperatures produces almost no valuable products[17] except montan wax and this is obtained more cheaply from lignites. "Solvent extraction" is frequently used erroneously to describe high-temperature treatment which simultaneously depolymerizes and hydrogenates the coal, properly, most solvent processing of coal should be called solvolysis [see "Solvent Refined Coal (SRC)," Chap. 1]. Dow Chem. Co.[18] has experimented with caustic oxidation, obtaining high-molecular-weight polyfunctional aromatic coal acids, which have found limited use in thermosetting resins and water-soluble films. Sulfur[19] recovery from coal is difficult but increasing

[16]Franck, The Challenge in Coal Tar Chemicals, *Ind. Eng. Chem.* 55 (5) 38 (1963); many coal chemicals described. West, Nonfuel Chemicals from Coal, *Ind. Eng. Chem.* 62 (1) 28 (1970).

[17]Future for Fossils, *Chem. Week* 115 (15) 46 (1974).

[18]Montgomery, Coal Acids, *Chem. Eng. News* 37 (37) 96 (1959); Perry, op. cit.; Burke op. cit.

[19]Manderson, The Emerging Sulfur Outlook, *Chem. Eng. Prog.* 72 (7) 25 (1976).

In countries that lack the sulfur raw materials found in the United States (H_2S from gases and sulfur from salt domes), pyrite has been recovered from coal and is used to the extent of about 10,000 t yearly in England and Germany. Sulfonation[20] has been employed to a limited extent to manufacture ion-exchange resins for water softening.

HYDROGENOLYSIS (HYDROGENATION-PYROLYSIS). Many developmental investigations[21] have been carried out on direct and catalytic hydrogenation of coal both in the United States and abroad. Most of these processes are really hydrogenolysis or hydrogenations (methanation) of the pyrolysis products of coal. They were designed to yield a gas with a high heating value to compete with natural gas, or to make motor fuel in petroleum-poor countries. The results gave such a gas, but at a high cost with much of the coal left as residual carbon. The motor fuel objectives were mostly for wartime demands except in South Africa.[22]

The present attack on coal to secure other and hopefully cheaper coal chemicals tends to follow catalytic hydrogenation and other processing, often grouped together as "coal refining" and combined with liquid separation, coking, and hydrocracking in the presence of hydrogen, without aiming for the uneconomical total hydrogenation of the carbon.

COAL RESEARCH. Various U.S. government agencies have been encouraging research on coal preparation and utilization, including chemical utilization. Investment in this work is shifting from government to private industry as the feeling of urgency becomes less and the energy crisis becomes less acute and more familiar. The energy crisis of 1973 to 1974, the increasing U.S. demand for fuel, and the fourfold rise in the cost of oil improve the outlook for coal as a feedstock in place of oil.[23] It appears that it will be only a question of time until coal replaces a significant amount of oil as feedstock in the United States. Conversion of the economy from a petroleum base to a coal base will require an investment in plants much greater than the current investment in the petroleum industry. The scope of such a change staggers the imagination.

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[20]Broderick and Bogard, *U.S. Bur. Mines Rep. Invest.*, 3559, 1951; Lowry, op. cit., p. 1091.

[21]Farber, Pipeline Coke-Oven Charging, *Chem. Eng.* 80 (29) 26 (1973).

[22]South Africa Banks on Coal for Chemical Buildup, *Chem. Week.* **115** (13) 33 (1974).

[23]Chemicals from Coal: Best Bet in Energy Crisis, *Chem. Week.* **114** (24) 11 (1974); The Coke Oven Revisited, *CHEMTECH* **5** (10) 618 (1975).

Chapter 3

Fuel Gases

During the 1950s a deep and far-reaching change took place in the fuel-gas industries, involving the domination of these widespread markets by natural gas. This was made economical through the countrywide installation of gas pipelines, reaching from large gas fields to most homes and factories in the United States. Local peak demands in winter are satisfied by the use of natural gas stored in neighboring underground depleted production wells, by the use of liquefied natural gas (LNG), by the use of liquid petroleum gas (LPG), or by peak production. LPG also meets needs in areas that pipelines cannot reach. The convenience, cleanliness, and reasonable price of natural gas have been a boon to Americans. This change has competitively restricted coke-oven gas to those areas where coke is made from coal for the steel and foundry industries (Chap. 2). This competition has reduced water gas mostly to use in the making of peak gas and synthesis gas (Chap. 4). Producer gas and retort coal gas have almost disappeared in the United States.

The need for a gas-from-coal process for peak shaving was eliminated in the late 1960s with the general acceptance of LNG as a safe method for storing natural gas for peak shaving where underground storage was not available. A propane-air system continues to be used during periods of high demand when only relatively small volumes of additional gas are required. Table 3.1 summarizes the composition and heating values of fuel gases. The choice in any case involves the composition, heating value, and cost of producing and distributing the gas. The heat content of a gas is a summation of the heats of combustion of its constituents and can be very accurately calculated from these values. Table 3.2 lists the individual heats of combustion and explains the variation in the heats of combustion of the gases given in Table 3.1.

HISTORICAL. The first recorded use of combustible gas was in about A.D. 900, when the Chinese piped natural gas through bamboo tubes and used it for lighting. The first production of coal gas took place about 1665, in England, and its first utilization was for lighting purposes in 1792. Similar endeavors in this country began in Philadelphia about 1796. It was not long after this that gas companies began to be organized and the manufacture of gas was put on a businesslike basis. The discoveries of water gas, or *blue gas*, in 1780, and of producer gas were essential steps in the development of this industry. The tremendous exploitation of our natural-gas fields gave the final impetus to the gas industry as we know it today.

This exploitation, however, has finally resulted in local natural-gas shortages, which began to appear in 1968. In that and following years, the volume of natural gas produced from wells was greater than the volume of new gas discovered. Because of this reduction in proved natural-gas reserves, exploration for gas on land and offshore increased. Some LNG is being exported from and imported into the United States in specially built ships over distances of more than 6400 km. The exports, contracted for before our shortages occurred, will not increase, but the imports will increase considerably. A few plants for gasifying petroleum

Table 3.1 Percent Composition and Heating Values of Various Fuel Gases*

Fuel Gas	Natural Gas (mid-continent)	Natural Gas (Pennsylvania)	Coke-Oven Gas	Blue Water Gas	Carbureted Water Gas	Bituminous Producer Gas
Carbon monoxide	—	—	6.3	42.8	33.4	27.0
Carbon dioxide	0.8	—	1.8	3.0	3.9	4.5
Hydrogen	—	—	53.0	49.9	34.6	14.0
Nitrogen	3.2	1.1	3.4	3.3	7.9	50.9
Oxygen	—	—	0.2	0.5	0.9	0.6
Methane	96.0	67.6	31.6	0.5	10.4	3.0
Ethane	—	31.3				
Illuminants	—	—	3.7	—	8.9	
Gross MJ/m^3	36	46	21	11	20	5.5

*Extensive tables, tables 9-15, 9-16, 9-18, and 9-19, are given by Perry where more properties are tabulated.

Table 3.2 Heats of Combustion of Common Natural Gas Constituents

Substance	MJ/m^3	Btu/ft^3
Methane	37.56	1000
Ethane	65.80	1763
Propane	93.65	2510
Butane	121.18	3248
Pentane	149.00	3752

SOURCE: ECT, 3d ed., vol. 11, 1980, p. 636.

products are operating, but their number will be limited because of oil shortages and high oil prices. Several coal-to-gas plants are being planned. These plants (oil and coal) will make pipeline-quality gas with about 37 MJ/m^3.

New processes for the production from coal of clean gas with about 5.5 MJ/m^3 are being planned. Methods for gasifying oil shale, solid municipal waste, sewage, animal waste, waste wood products, and material that can be grown for the purpose, such as trees and algae, are also being investigated. The United States has just started to use manufactured gas to supplement its still very large reserves of natural gas. The new gasification processes[1] being considered will gasify more of the organic material in coal than the old processes.

NATURAL GAS

Not only is natural gas the predominating fuel gas, but it has become a most important chemical raw material for various syntheses. These will be presented in Chap. 38, Petrochemicals, as well as elsewhere in this book, so fundamentally important has natural gas become (Chaps. 4, 5, 18). For example, in 1979 the chemical process and allied industries used 6.38×10^9 MJ, and the carbon black and lampblack industry used 32.7×10^9 kJ as natural gas (approximately 37 MJ/m^3). Most large chemical companies have established plants in Texas or Lou-

[1]Conn, Conversion of Coal to Oil and Gas, *Chem Eng. Prog.* 77 (5) 11 (1981).

isiana near or right on the gas fields, to supply the chemical processes with the cheapest possible natural gas

USES AND ECONOMICS. The proved recoverable reserves[2] of natural gas in the United States were at a maximum at the end of 1967 when they were 8.3×10^{12} m^3. At the end of 1980 they had declined to 5.4×10^{12} m^3. Gas production peaked in 1974 with 6.3×10^{11} m^3 being produced. In 1980 only 5.7×10^{11} m^3 were produced, which constituted 34 percent of world production. It is predicted[3] that by the year 2000 the supplies will decline to 4.5×10^{11} m^3, and the demand will increase to 7.3 to 9.3 $\times 10^{11}$ m^3. This will necessitate a large increase in imports and synthetic gas production

Of the 15.8×10^9 MJ sold to customers in 1979, residential sales were 5.4×10^9 MJ, commercial sales were 2.6×10^9 MJ, and industrial sales amounted to 7.98×10^9 MJ. The average residential customer paid $2.76 per gigajoule; the commercial customer, $2.52 per gigajoule; and the industrial customer, $2.12 per gigajoule. The average price of natural gas at the wellhead in 1979 was $1.08 per gigajoule. In 1972 the cost for the same amount of gas was only $0.165. As long as inflation continues, the cost of gas will continue to rise sharply from year to year.[4]

Various products from raw natural gas are of industrial significance, such as methane, ethane, propane, butane, LPG, and natural gasoline. For helium, see Chap. 4. In view of the increased value of natural gas, processes used to recover these products are becoming more fuel efficient. Many older plants use a refrigerated oil absorption process operating in the range of -18 to -40°C. To achieve additional fuel conservation, modern technology calls for the use of the cryogenic-expander process operating at temperatures in the range of -90 to -100°C. After expanding the gas down to pressures of 1380 to 2415 kPa, the residue gas may require recompression to the higher pressure required for sale. This process may use 30 to 40 percent less fuel than the refrigerated oil absorption process. After the condensed liquids are separated from the gas stream they may be fractionated under pressure to separate products as required for sale. Fuel usage may be further reduced by recovering waste heat from gas engine and turbine exhaust gases, and heater vent gases. Fuel gases are marketed throughout the United States in steel cylinders, tank trucks, tank cars, and special sea-going vessels. The separation and utilization of natural gasoline, or *casing-head* gasoline, as it is often called, will be presented under petroleum refining in Chap. 37.

DISTRIBUTION. After necessary purification, which will be described, natural gas is compressed to about 6.9 MPa and sent through transmission mains which form a network throughout the country. It is recompressed by gas compressors driven by various prime movers, frequently gas engines or turbines. As it nears the consumer, the distribution pressure is reduced to as low as 200 to 600 Pa at the gas appliance. This natural gas is employed as fuel or raw material in cities throughout the country, some cities being 3000 km or more from the producing wells. The natural-gas distribution system in this country now involves 1.6×10^7 km of transmission and distribution pipelines. Ships and tank trucks transport LNG to distant markets and to those not reached by pipelines. The whole natural-gas industry in this country has a plant investment of $75,000 million, much of which is in pipelines.

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[2]ECT, 3d ed., vol. 11, 1980, p. 631.

[3]Wett, Gas Processing, *Oil Gas J.* **79** (28) 67 (1981); Gas Shortfall Seen Possible, *Oil Gas J.* **79** (37) 53 (1981).

[4]*1979 Gas Facts*, American Gas Association.

PEAK DEMANDS.[5] It is not unusual for the winter natural-gas load for a company to be several times that of its summer load, so it is desirable to be able to store gas near densely populated areas to be used during periods of high demand. The best procedure, widely practiced, is to store natural gas underground in depleted oil or gas reservoirs, at pressures that existed when the well was first drilled (as high as 2.7 MPa), or in aquifers where the displaced water acts as a seal. This stored gas is withdrawn when needed. Natural gas is also liquefied, at −160°C, to obtain a 600:1 volume reduction, and stored, usually in above-ground double-walled insulated steel containers. During periods of high demand it is vaporized and distributed. To a limited extent, it is possible to vaporize stored propane, mix it with air, and add the mixture to natural gas as another method of peak shaving. When mixing gases, the combustion properties of the final composition must always be considered.

NATURAL-GAS PURIFICATION.[6] In addition to the industrially valuable propane and butane, raw natural gas contains undesirable water and hydrogen sulfide which must be removed before it can be placed in transmission lines. Four important methods are employed for the dehydration of gas: compression, treatment with drying substances, adsorption, and refrigeration. A plant for water removal by compression consists of a gas compressor, followed by a cooling system to remove the water vapor by condensation. The treatment of gas with drying substances has found widespread usage in this country. Glycols are used most widely for this purpose because of their high affinity for water, low cost, chemical stability, low foaming, and low solvent action for natural gas. For water dewpoints in the range of −90 to −100°C, molecular sieves are used in many plants. The beds are regenerated by countercurrent flow of hot gases (230 to 290°C).

Other drying agents are: activated alumina and bauxite, silica gel, sulfuric acid, and concentrated solutions of calcium chloride or sodium thiocyanate. Plants of this type usually require a packed tower for countercurrent treatment of the gas with the reagent, together with a regenerator for the dehydrating agent. Gas may also be dehydrated by passing it over refrigerated coils. In general, this method is more costly than the others but, where exhaust steam is available to operate the refrigeration cycle, refrigeration charges can be reduced. If the water present in most fuel gas is not removed, unduly high corrosion will occur in the transmission lines, and trouble may also result from the formation of hydrates, which can cause line stoppages. The freezing of valves and regulators in cold weather may also cause difficulties.

Hydrogen sulfide and other sulfur compounds are objectionable in natural gas because they cause corrosion and also form air-polluting compounds when burned. The odor of hydrogen sulfide is very annoying to household customers. Recent stringent air-pollution laws require the removal of sulfur compounds before the gas is fed into the distribution system. Carbon dioxide in the gas is objectionable because it lowers the heating value of the gas. In raw natural gas, the amount of H_2S present may range from 0 to 35 g/m^3 or higher. Table 3.3 summarizes the important commercial processes that are being used to remove H_2S and CO_2 from gas. The sulfur compounds removed from the gas are usually converted to elemental sulfur by modifications of the Claus process (see Chap. 19).

Monoethanolamine is the oldest and probably still the most widely used solvent. A flow-

[5]Peak Shaving Report, *Pipeline Gas J.*, Dec. 1973, pp. 25–30.

[6]Zawecki, Duncan, and Macriss, Process Optimized for High Pressure Gas Cleanup, *Hydrocarbon Process*, **60** (4) 143 (1981); New Gas Sweetening Process Offers Economical Alternative, *Oil Gas J.* **79** (35) 60 (1981).

***Table* 3.3** Carbon Dioxide and Sulfur Removal Processes

Process or Reagent	Trade Name
Chemical Solvent in Aqueous Solution	
Monoethanolamine (MEA)	Girbotol
MEA plus amine guard	Ucar
Diethanolamine (DEA)	
Diglycolamine	Fluor Econamine
Diisopropanolamine	Shell[a]
Hot potassium carbonate	Benfield, Catacarb, Giammarco-Vetrocoke
N-Formyl morpholine	
Slurry of highly reactive iron compound	Slurrisweet
Physical Solvent	
Methanol	Rectisol
Propylene carbonate	Fluor
Poly(ethylene)glycol dimethyl ether	Selexol
Tetrahydrothiophene-1,1-dioxide	Shell Sulfolane[a]
N-Methyl-2-pyrrolidone	Purisol
Dry Bed of Solid, Granular Material	
Hydrated iron oxide coated wooden chips (iron sponge)	

[a]This process uses both types of solvents and the combination reagent is called Sulfinol

SOURCE: ECT, 3d ed., vol. 11, 1980, pp. 638–641; vol. 4, 1978, pp. 733–736; vol. 2, 1978, p. 493

chart is presented for this procedure in Fig. 3.1. For desulfurization of natural gas, a 10 to 30% aqueous solution of monoethanolamine is normally used. The various solvents listed in Table 3.3 vary in their selectivity for absorption of H_2S and CO_2 and this property, as well as the composition of the impurities in the gas being treated, frequently determines the choice of solvent. Some of the solvents also have a high affinity for higher hydrocarbons, and this is a disadvantage if the gas contains an appreciable quantity of these valuable compounds. If simultaneous dehydration and desulfurization is desired, the gas may be scrubbed with a solution of amine, water, and glycol. Solution compositions for this purpose are from 10 to 36% monoethanolamine, 45 to 85% diethylene glycol, and the remainder water.

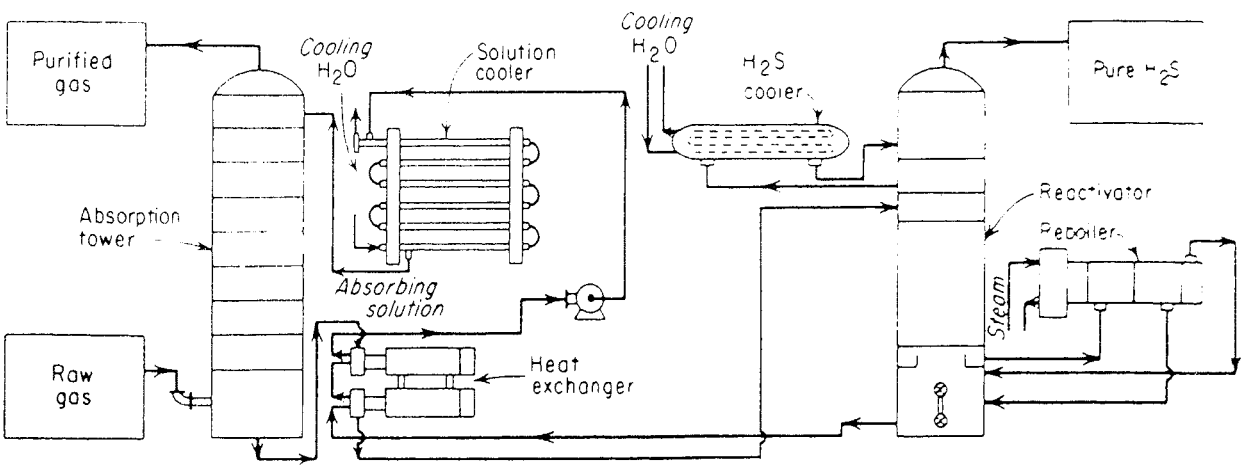

Fig. 3.1. Gas purification by the aliphatic amine absorption process.

One of the newest commercial methods of sweetening gas is the use of membranes.[7] This separation works on the principle that there are different rates of permeation through a membrane for different gases. Membrane materials used are polysulfone, polystyrene, Teflon, and various rubbers. This type of separation possesses many advantages over other types of gas separation, e.g., mild operating conditions, lower energy consumption, low capital cost, and economic operation at both low and high flow rates.

Natural gas with a high nitrogen content can be upgraded by a cryogenic process which dries feed gas at 4.9 MPa and cools it to 185 K. The natural gas is vaporized, and both this and the separated nitrogen gas leave the system via heat exchangers against incoming gas.[8]

COKE-OVEN GAS

Coke-oven[9] gas is now only produced as a by-product. The processes for the distillation of coal are discussed in Chap. 2. The following is merely an outline of the treatment of gas obtained from chemical-recovery coke ovens. The by-products in the hydraulic main first go via the foul main through a primary condenser and a baffled tar extractor, as shown in Fig. 2.3, where the coke-oven gas[10] is separated from the ammonia liquor and the coal tar. The gas has its ammonia removed as ammonium sulfate by bubbling through sulfuric acid. Coal-tar products such as benzene, toluene, and some naphthalene are scrubbed by straw oil in a packed light-oil tower or scrubber. The uses of coke-oven gas are largely for fuel gas in the many steel-plant operations with which almost all U.S. coke-oven plants are associated. Some of the gas may be used for underfiring the coke ovens themselves. In a few localities coke-oven gas is purified and sold to the local utility company for distribution to the community.

PRODUCER GAS[11]

Producer gas is made by passing air and steam through a bed of hot coal or coke. The allowable temperature of the fuel bed, which depends on the fusion points of the fuel ash, usually ranges from 980 to 1540°C, and the minimum bed height ranges from 0.6 to 1.8 m for most of the commonly used fuels. The primary purpose of the steam (25 to 30 percent of the weight of the coke) is to use up, as much as possible, the exothermic energy from the reaction between carbon and oxygen to supply the endothermic reaction between the carbon and the steam.

$$C + \text{air} \rightarrow CO_2 + N_2 \qquad \Delta H_{1000°C} = -395.4 \text{ MJ/kg mol} \qquad (1)$$

$$CO_2 + C \rightarrow 2CO \qquad \Delta H_{1000°C} = +167.9 \text{ MJ/kg mol} \qquad (2)$$

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H_{1000°C} = +135.7 \text{ MJ/kg mol} \qquad (3)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_{1000°C} = -32.18 \text{ MJ/kg mol} \qquad (4)$$

[7]Membranes Separate Gas, *Chem. Eng.* 88 (14) 63 (1981).

[8]*Gas Processing Handbook*, Hydrocarbon Processing, April, 1979, p. 124.

[9]Retort coal gas is still made and used in Europe, but not in the United States.

[10]Operating results on coal gas are given in Lowry, *The Chemistry of Coal Utilization*, Suppl. Vol., Wiley, New York, 1963, p. 892.

[11]Berkowitz, *An Introduction to Coal Technology*, Academic, New York, 1979, p. 25.

The initial reaction is the formation of CO_2 and N_2 (1). As the gases progress up the bed, the initial CO_2 is reduced to CO (2), and the water vapor (made from the liquid water in jacket) is partly decomposed to yield H_2, CO, and CO_2 (3), (4). Producer gas has about 15 percent of the heating value of natural gas. It was once used for industrial heating, but its use in the United States is now almost obsolete

WATER GAS (Blue Gas)[12]

Water gas is often called *blue-gas* because of the color of the flame when it is burned. It is produced by the reaction of steam on incandescent coal or coke at temperatures above 1000°C. The following reactions occur:

$$C + H_2O \rightarrow CO + H_2$$
$$C + 2H_2O \rightarrow CO_2 + 2H_2$$

The heating value of this gas is low (Table 3.1) and, to enhance it, oil may be atomized into the hot gas to produce *carbureted* water gas, which has a higher heat content.

SYNTHESIS GAS (Syngas)[13]

Modern processes have been developed to produce a $CO-H_2$ mixture from coal and steam more efficiently than the old water-gas and producer-gas plants. The gases produced are of low heat content (3.7 to 7.5 MJ/m^3) if steam and oxygen are used. The principal difference between the low-heat gas and the medium-heat gas is that the 3.5 to 7.5 MJ/m^3 gas contains about 50% nitrogen, which enters the system as part of the air. The low-heat gas is used mainly as an on-site industrial fuel and as an intermediate in the production of formaldehyde and ammonia, while the medium-heat gas can be economically transported by pipeline for distances of 160 to 320 km. Much of the gas is methanated to produce substitute natural gas (SNG).

The types of gasification systems are classified according to gasifier bed type: fixed bed, fluidized bed, and entrained bed. The oldest examples of these are the Lurgi process (fixed bed), Winkler process (fluidized bed), and Koppers-Totzek process (entrained flow). All of these processes have been commercially used worldwide, although none have been commercially operated in the United States. Efforts to create improved reactors for very large scale SNG production (daily throughputs of 5000 to 10,000 t of coal[13a]) have led to the development of several so-called *second-generation* reactors, which are usually modifications of these older processes (Table 3.4)

The Lurgi process has a pressurized (up to 2800 kPa) moving-bed system that cannot use strongly caking coals and that operates with either air or oxygen. Noncaking coals found in

[12]Parker, A Thermal Study of the Process of Manufacture of Water Gas, *J. Soc. Chem. Ind. London* 46 721 (1927).

[13]Patel, Low, Medium-Btu Gas from Coal Lead Conversion Routes, *Oil Gas J.* 79 (26) 90 (1981); Haase, Duke, and Cates, CO Recovery and Purification, *Hydrocarbon Process.* 61 (3) 103 (1982); Tucci and Streeter, *Hydrocarbon Process.* 59 (4) 107 (1980); Low-Btu Fuel from Small Coal Gasifiers, *Chem. Week* 130 (22) 28 (1982).

[13a]t = 1000 kg.

Table 3.4. Coal Gasification Process Technology Status—1981

Gasifier	Technology	Coal Feed, t/day	Location	Status
Fixed Bed				
Lurgi-Dry Ash	1st generation		Worldwide	Commercial
British Gas/Lurgi Slagging	2d generation	600–800	Westfield, Scotland	Will begin operation 1982
		3800	Noble County, Ohio	Complete engineering design 1981
ATC/Wellman	2d generation	200	York, Pa.	On stream in 1979
Fluidized Bed				
Hygas	2d generation	75	Chicago, Ill.	Started in 1972
U-Gas	2d generation	2800	Memphis, Tenn.	Detailed design 1982
Entrained Bed				
Koppers-Totzek	1st generation		Worldwide	Commercial
Texaco	2d generation	150	Germany	Started in 1978
		1000	Barstow, Calif.	In design stage
		200	Muscle Shoals, Ala.	Test operation 1980
		1600	Kingsport, Tenn.	Scheduled for 1983
Shell-Koppers	2d generation	150	W. Germany	Obtaining data for larger plant
Combustion Engineering	2d generation	150	Windsor, Conn.	Started up in June 1978

the western United States should cause few problems. Sized coal is fed at the top of the gasifier and steam or oxygen are injected at the bottom (Fig. 3.2). The temperature of gasification is lower than with the other types of beds. As the coal gravitates downward and is heated, devolatilization commences and, from a temperature of 620 to 760°C upward, devolatilization is accompanied by gasification of the resulting char. The crude gas leaves the gasifier at temperatures between 370 and 595°C, depending upon the type of coal. It contains carbonization products such as tar, oil, naphtha, phenols, ammonia, and traces of coal and ash dust. This crude gas is passed through a scrubber where it is washed by circulating gas liquor and then cooled to a temperature at which the gas is saturated with steam. The gas leaving the gasifier is mainly CO_2, CO, CH_4, H_2, and H_2O.

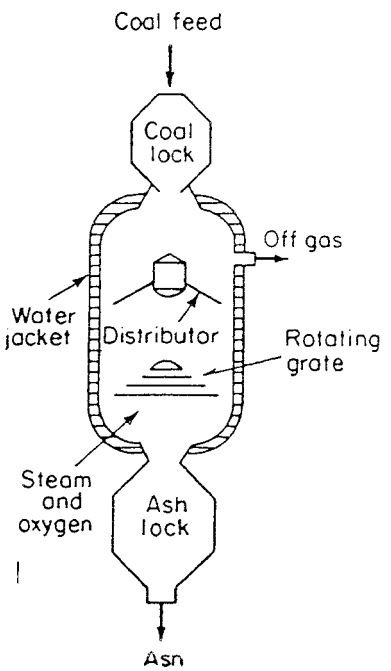

Fig. 3.2. Lurgi pressure gasifier.

The Winkler fluidized bed gasifier has the advantage of uniform temperature distribution and excellent solid-gas contact. Crushed or fine coal is fed into the top and oxygen and steam into the bottom, as shown in Fig. 3.3. It can handle a wide variety of coals without a significant loss of efficiency. Caking coals, however, must be pretreated before being fed to the process. Operating temperatures (800 to 1000°C) are higher than for the entrained bed. The exit gases have a high dust content and must be treated to remove the dust. Several modifications have been made in the original Winkler process. These are the Hygas, U-Gas, Westinghouse, and Cogas. The Hygas and U-

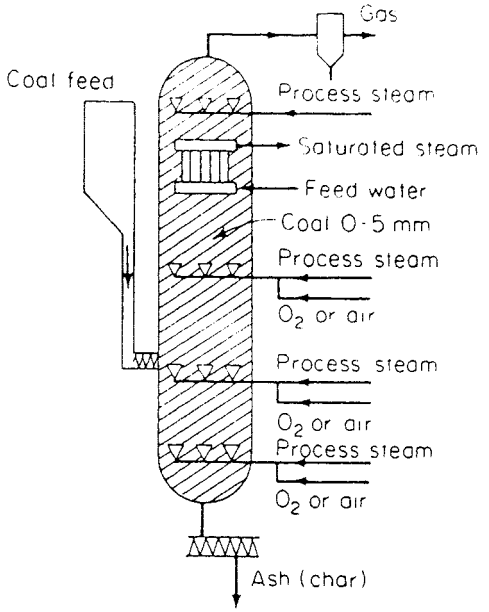

Fig. 3.3 Winkler generator fluidized bed gasifier.

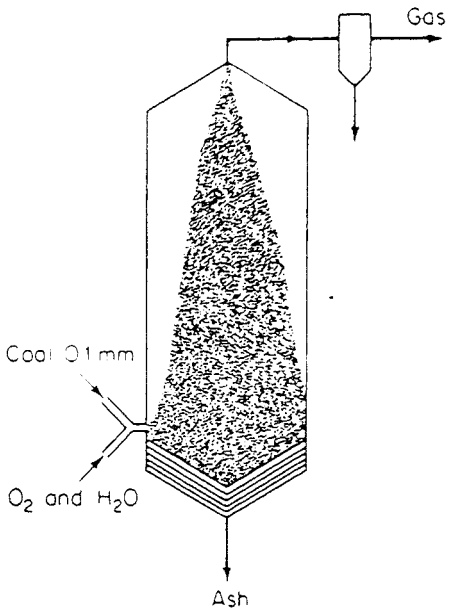

Fig. 3.4. Entrained suspension coal gasification.

Gas processes were developed by the Institute of Gas Technology in Chicago, and Cogas was developed cooperatively by the FMC Corporation and the British National Coal Board.

The Koppers-Totzek entrained bed gasifier has the highest capacity per unit volume of the three processes. The pulverized coal, oxygen, and steam are fed together and the coal is gasified in suspension (Fig. 3.4). It has the ability to handle all types of coals and produces a gas free of tars and phenols. However, it requires high temperatures (1900°C) and large amounts of oxygen. No pretreatment of caking coal is required as the flowing gas separates the particles, and they are gasified so rapidly that they cannot agglomerate. The overall gas production rates are higher than either the fixed bed or entrained bed.

***Table* 3.5** Composition of Typical Product Gases (dry basis) (mole percent)

	Lurgi	Koppers-Totzek	Winkler
H_2	38.0	36.7	41.8
CO	20.2	55.8	33.3
CO_2	28.6	6.2	20.5
CH_4	11.4	0.0	3.0
C_2H_6	1.0	0.0	0.0
H_2S or COS	0.5	0.3	0.4
N_2	0.3	1.0	1.0

Table 3.5 shows typical gas compositions for these three processes. All of these gasification processes have been in use throughout the world, especially in Germany, for many years. In 1981 there was only one small plant using second-generation technology operating in the United States, the Caterpillar Tractor Co. plant in York, Pa. This is a fixed bed gasifier. Tennessee Eastman has a plant under construction at Kingsport, Tenn. to produce synthesis gas using the Texaco second-generation, entrained bed process. It is scheduled to start production in 1983. Many active projects are in various stages of planning and/or construction.[14]

[14]Schwartz, Rath, and Freier, The Westinghouse Gasification Process, *Chem. Eng. Prog.* 78 (4) 55 (1982); Kuhn, The Great Plains Gasification Project, *Chem. Eng. Prog.* 78 (4) 64 (1982); Coal Gasifier Operated Successfully, *Chem. Eng. News* 60 (21) 33 (1982).

SUBSTITUTE NATURAL GAS (SNG)

Coal Gasification

The low- and medium-heat syngas produced from coal can be converted to a high-heat content gas (30 to 37 MJ/m^3) similar to natural gas by the following reactions:

$$C + H_2O \rightarrow CO + H_2 \quad \text{gasification} \quad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{water gas shift reaction controlled to give } CO:H_2 = 1:3 \quad (2)$$

$$C + CO_2 \rightarrow 2\,CO \quad \text{Boudouard reaction} \quad (3)$$

At sufficiently high pressures the hydrogen from reactions (1) and (2) will hydrogenate some of the carbon to yield methane.

$$C + 2H_2 \rightarrow CH_4 \quad (4)$$

$$CO + 3H_2 \xrightarrow{\text{catalyst}} CH_4 + H_2O \quad \text{methanation} \quad (5)$$

The gas thus produced was known originally as synthetic natural gas, but language purists argued that synthetic could not be natural, so now it is called *substitute natural gas*. The sulfur and carbon dioxide are removed from the gas before it is methanated. The operating pressure in the gasifier, depending upon the process, can be atmospheric to over 6.9 MPa, and the temperature can vary from 800°C to about 1650°C. The higher pressure and lower temperature result in the formation of a larger amount of methane. Figures 3.5 and 3.6 show a flow sheet for the gasification of coal to produce SNG, and the equations and gasifier involved.

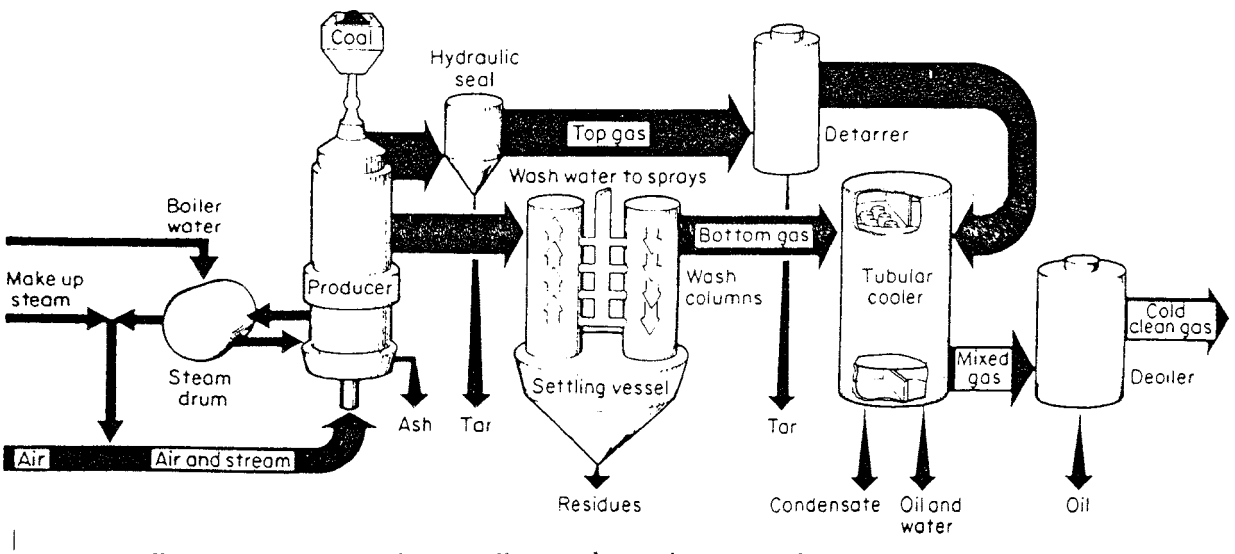

Fig. 3.5. Wellman two-stage gasifier *(Wellman Thermal Systems Corp.)*

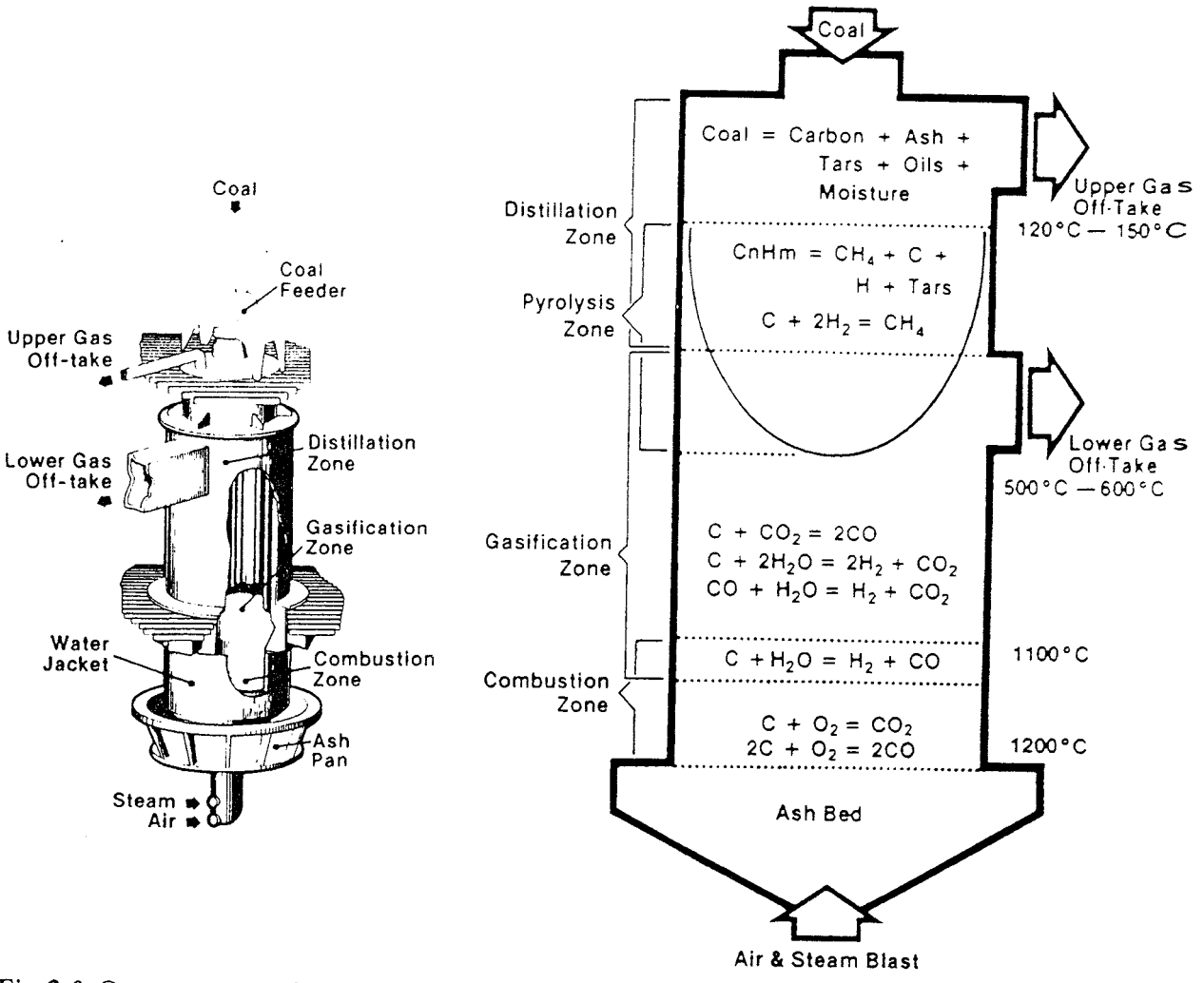

Fig. 3.6. Cut away view of two-stage gasifier and chemical reactions *(Wellman Thermal Systems Corp.)*

Oil Gasification

Naphtha and other oils can be converted to SNG, but most of the cost of the product gas is due to the cost of the oil. Thus, the cost of gas produced from oil is so high that it is not now competitive with gas produced from coal. The processes used mix naphtha with steam in a 1:2 ratio and gasify the mixture. The gas produced is methanated by the reaction of the carbon oxides with the hydrogen present. Purification requires the removal of any residual carbon dioxide

LIQUEFIED PETROLEUM GASES (LPG)

Liquid propane and butane gas are employed as standby and peak-load supplements in municipal and industrial systems using natural and manufactured gas, and as a complete gas supply in some communities and industries. LPG is used for flame weeding, tobacco curing, grain drying, and in motor vehicles and tractors. The petrochemical industry is the second largest consumer (Chap. 38). Since butane (121 MJ/m^3) does not vaporize below 0°C, it is preferred in the south, whereas propane (94 MJ/m^3) vaporizes down to −42°C and is used

in the north. Sometimes a mixture of these two is employed. LPG comes from the ground as a constituent of wet natural gas or crude oil or as a by-product from refining. For example, a natural gasoline plant treats raw "wet" natural gas through absorption by "washing" with gas oil and fractionating out the usable fraction. It is expected that LPG will continue to provide less than 5 percent of the total U.S. energy supply. This includes its use in gasoline blending.

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Chapter 4

Industrial Gases

Industrial gases perform varied and essential functions in our economy. Some are raw materials for the manufacture of other chemicals. This is particularly true of oxygen, nitrogen, and hydrogen. Nitrogen preserves the flavor of packaged foods by reducing chemical action leading to rancidity of canned fats. Some gases are essential medicaments, like oxygen and helium. However, many of these gases, their liquids, and their solids have a common application in creating cold, by absorbing heat upon evaporation, by performing work, or by melting. In past decades, the outstanding examples of this have been liquid carbon dioxide and dry ice. On the other hand, with the modern expansion of industry, a new division of engineering has arisen called *cryogenics*.[1] This widely embracing term pertains to the production and use of extreme cold at temperatures below −100°C. The term has been applied very extensively during the last decade and is exemplified by the use of liquid hydrogen, oxygen, and fluorine in missiles for military and space projects. New cryogenic techniques have been worked out, reducing the cost of liquefaction, and improving and simplifying the equipment used for storage, handling, and shipment of very cold liquids and gases. The economic advantage of using cryogenic liquids is apparent when it is realized that a cylinder weighing 113 kg contains 169 kg of liquid oxygen (equivalent to 126 m^3 of gaseous oxygen at normal temperature and pressure). Eighteen small cylinders of gaseous oxygen contain a total of 166 kg of oxygen gas at a pressure of 15 MPa, but they weigh 1090 kg. Cryogenic liquids are stored and shipped in tanks or large tank cars[2] built on the multiple-walled vacuum bottle (Dewar) principle. The value of cryogenic[3] gases, oxygen, nitrogen, argon, helium, and hydrogen (merchant only), amounted to $1250 million in 1980. Of that total, oxygen accounted for $500 million, nitrogen $450 million, and hydrogen $110 million.

These cryogenic, or supercold, temperatures cause fundamental changes in properties of materials. Cryogenics is being applied to rocket propulsion, infrared photoptics, and electronic data processing, with newer applications in magnetics and high-vacuum pumping. The major application of cryogenics to the chemical field is in the manufacture of nitrogen for ammonia production, and in metallurgy, where the use of oxygen hastens (by 25 percent or more) the production of steel in open-hearth furnaces, converters, and even in blast furnaces for pig iron. Cryogenics,[4] in manufacturing low-temperature liquids, has long applied the

[1]From the two Greek words meaning "the making of cold."

[2]New Tank Car Hauls Liquid H_2 from Florida to California, *Chem. Eng.* 69, 18, 66, 1961.

[3]Courtesy of Linde Division, Union Carbide Corp.

[4]See Perry, p. 11-10, 11-48 to 11-52, 12-49 to 12-53.

following *fundamental principles*, and currently, most extensively to air and its constituents:

1. Vapor compression with liquefaction if below the critical temperature of the gas in question
2. Interchange of heat in heat exchangers such as double-pipe units; refrigeration
3. Cooling of compressed gases by allowing them to perform work in expansion engines or turbines
4. Cooling of the liquids by evaporation
5. Separation of gases by difference in vapor pressure at the boiling point of the liquid mixture
6. Removal of contaminants by adsorption, freezing on surfaces, freezing followed by filtration of the cryogenic liquid, or by washing with an appropriate liquid

CARBON DIOXIDE

Carbon dioxide in liquid and solid forms has been known for over a century. Although Thilorier produced solid carbon dioxide in 1835 from the liquid material, it was not until 1924 that the solid product gained industrial importance through its first and still most important use for refrigeration. The production of merchant carbon dioxide in 1981 was about 3.6×10^6 t total for the gaseous, liquid, and solid forms.[4a]

USES.[5] By far the largest use of the solid form is for refrigerating and freezing ice cream, meat, and other foods. An added advantage is that a carbon dioxide atmosphere reduces meat and food bacteria spoilage. The solid form is also important as a source of carbon dioxide for inert atmospheres and occasionally for carbonated beverages. There are many other specialty uses, such as chilling aluminum rivets and shrink-fitting machine parts. The largest outlet of liquid carbon dioxide is for carbonated beverages. It is also important as a fire-extinguishing material. Gaseous carbon dioxide has many applications in the chemical industry, such as in the making of salicylic acid (Chap. 40).

Carbon dioxide has advantages over ordinary acids in neutralizing alkalies, because it is easily shipped in solid form, is noncorrosive in nature, and is light in weight. Chemically, it is equivalent to more than twice its shipping weight in sulfuric acid and about five times its weight in hydrochloric acid. It is finally gaining acceptance for pH control of wastewater after this use had been talked about for years.

With respect to food refrigeration, solid carbon dioxide is primarily a transport refrigerant. Its advantages cannot be attributed to any single factor but result from its dryness, its relatively high specific gravity, its excellent refrigerating effect, its low temperature, and the insulating and desiccating action of the gas evolved. Generally, about 450 kg of solid carbon dioxide will refrigerate an average car for a transcontinental rail trip without recharging. See Table 4.1 for a comparison of the properties of solid carbon dioxide and water ice. Liquid nitrogen has also entered this refrigerating field. The uses for all forms of CO_2, both merchant and captive, are: 40 percent for the production of urea, 35 percent for pressurizing oil wells for secondary oil recovery, 10 percent for refrigeration, 5 percent for beverage carbonation, and 10 percent for miscellaneous uses.

[4a] t = 1000 kg.

[5] Yaws, Li, and Kuo, Carbon Oxides, *Chem. Eng.* 81 (20) 115 (1974); Key Chemicals, Carbon Dioxide, *Chem. Eng. News* 60 (29) 23 (1982).

***Table* 4.1** Comparison of Physical Properties of Solid CO_2 and Water Ice

Property	Solid CO_2	Water Ice
Specific gravity	1.56	0.90
Sublimation point or melting point, °C	−78.5	0
Critical temperature, °C	30.9	365.6
Critical pressure, GPa abs	7.38	19.72
Latent heat of fusion, kJ/kg	190.7	334.9
Latent heat of vaporization, kJ/kg	368.9	24.9×10^3
Weight of 1 m^3 of gas, kg	1.98	0.804
Weight of 1 m^3 of solid, kg	1441	913
Latent heat of sublimation, kJ/kg	576.8	
Refrigerating effect, kJ/kg	639.7	334.9

MANUFACTURE OF PURE CO_2.[6] Although there are many sources of CO_2, the following four are the most important for commercial production:

1. Recovery from synthesis gas in ammonia production
2. Recovery as a by-product in the production of SNG (see Chap. 3)
3. Recovery from the production of ethanol by fermentation (Chap. 31)
4. Recovery from natural wells

An absorption system is used for concentrating the CO_2 gas to over 99% purity. In all cases the almost pure CO_2 must be given various chemical treatments for the removal of minor impurities that contaminate it. One of the reversible reactions long used for the concentration of CO_2 is

$$Na_2CO_3 + CO_2 + H_2O = 2\ NaHCO_3$$

This reaction is forced to the right by increasing the partial pressure of the CO_2 and by reducing the temperature. It is forced to the left by heating the sodium bicarbonate solution. The absorption efficiency of 10 to 18% CO_2 is not very good. Other, usually more economical reversibly absorbing solutions are hot, concentrated potassium carbonate solution and monoethanolamine (Girbotol process, Chap. 3). The CO_2 available in these cases comes from the combustion of fuel oil in a boiler plant generating the required steam. To carry out this manufacture, the following principal sequences are employed:

Oil, natural gas, or coke is burned, giving heat for 1380 kPa steam and furnishing flue gas 13 to 15% CO_2 at 345°C.

Flue gas cooled, purified, and washed by passing through two water scrubbers.

CO_2 is removed by countercurrent selective absorption into an aqueous solution of ethanolamines.

CO_2-ethanolamine solution is pumped to a steam-heated reactivator.

CO_2 and steam leave the top of the reactivator passing through a CO_2 cooler to condense the steam, which returns to the tower as reflux.

[6]Perry, p. 16-36 and p. 16-42 for absorption of carbon dioxide; p. 3-162 for thermodynamic properties; ECT, 3d ed., vol. 4, pp. 725–742, 1978. Strelzoff, Choosing the Optimum CO_2-Removal System, *Chem. Eng.* 82 (19) 115 (1975).

CO_2 at about 200 kPa is purified from traces of H_2S and amines in a permanganate scrubber and dried.

CO_2 is compressed, cooled, and liquefied.

For "liquid" draw off from CO_2 receiver.

For dry ice:

Liquid CO_2 is reduced to atmospheric pressure, with consequent partial solidification. The evaporated gas returns through the precooler, and is recirculated, with recompression and recooling of CO_2.

CO_2 "snow" is compressed to form a cake.

Dry ice cakes are generally sawed to 25-cm cubes of approximately 23-kg weight.

A typical flowchart for continuously producing either liquid or solid and showing the sequences of these unit operations and chemical conversions is shown in Fig. 4.1. In the merchandising of liquid CO_2, the energy (hence expense) involved in handling the cylinders, full and empty, is so great that bulk cryogenic shipment of relatively low pressure liquid *cold* CO_2 is now being practiced to reduce container cost and weight. If heat exchangers are properly designed, it is necessary to buy little outside energy for solid CO_2 and none for liquid CO_2 (Fig. 4.1). The live steam generated by the boiler is sufficient to power the turbines for pumping and compression, and the exhaust steam from turbine-driven compressors boils off the CO_2 from the amine solution in the reboiler. The condensate from the reboiler is returned to the water boiler.

Another source of CO_2 is the fermentation industry, as described in Chap. 31. If yeast is used, alcohol and CO_2 are produced, and certain other microorganisms generate solvents and a gaseous mixture of H_2 and CO_2. The yield of CO_2 varies with the mode of fermentation. From 50 kg of starchy material such as corn, 17 L of 190-proof ethyl alcohol and 14 kg of CO_2 are obtained. The recovery and purification of CO_2 from fermentation differ from the absorption system in that the temperature seldom exceeds 40°C so that no special cooling is necessary and the CO_2 content of the gas usually starts above 99.5%. When the fermentors are sealed for the recovery of the gases, a purer and higher yield of CO_2 is obtained, and the yield of alcohol is increased by at least 1 percent by alcohol recovery from the CO_2 scrubbers.

A typical CO_2 recovery from fermentation is illustrated in the flowchart in Fig. 4.2. Here purification consists of oxidation of the organic impurities and dehydration by means of chemicals in liquid form. The gas from the fermentors is passed through three scrubbers containing stoneware spiral packing and on to the gasometer. The first scrubber contains a weak alcohol solution which acts as a preliminary purifier and removes most of the alcohol carried by the gas. The next two scrubbers, in which the scrubbing medium is deaerated water, remove almost all the water-soluble impurities. The scrubbing liquid is pumped either to the stills or to the fermentors for alcohol recovery.

From the gasometer the gas is conducted to a scrubber containing $K_2Cr_2O_7$ solution, which oxidizes the aldehydes and alcohols in the gas, and is then cooled. In the second scrubber, which contains sulfuric acid, oxidation is completed and the gas is dehydrated. The CO_2 leaving the acid scrubber contains some entrained acid which is removed in a packed tower over which a Na_2CO_3 solution is circulated. When the acid is neutralized, CO_2 is released. Before going to the compressor, the gas passes through a scrubber containing a small amount of glycerin, which absorbs the oxidized products and delivers an odorless gas to the compressor. The sulfuric acid, after being used for deodorization and drying, is pumped to the distillery, where it serves for pH control.

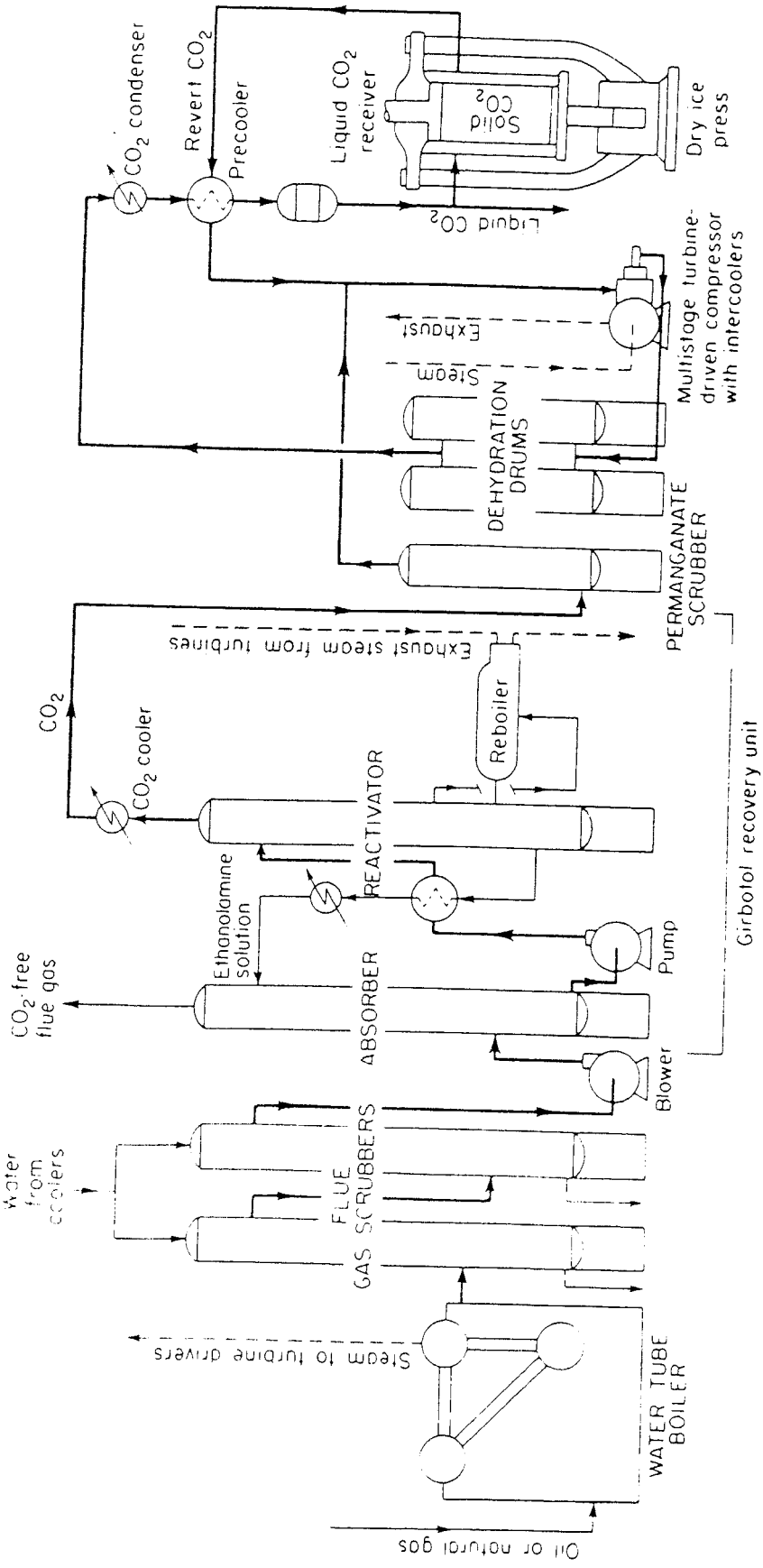
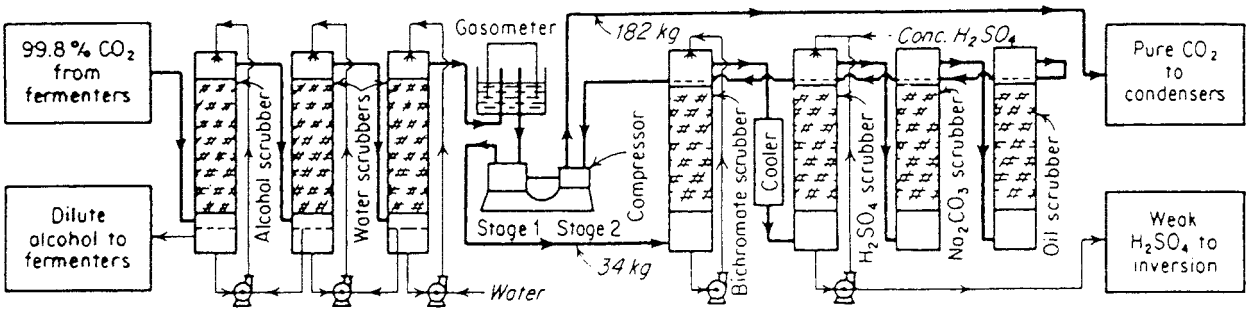


Fig. 4.1. Flowchart for CO_2 from fuel oil or natural gas *(Girdler Corp.)*



In order to produce 1 t solid CO_2, the following materials and utilities are required.

Bichromate	180 g	Water	7600 L
Sodium carbonate	4.5 g	Electricity	17.8 MJ*
Oil	0.04 L	Direct labor	0.1 work-h
H_2SO_4 (66°Bé)	19 L†		

Not including solid CO_2 compressing system.

†Weak H_2SO_4 all recovered for use in molasses fermentation.

Fig. 4.2. Flowchart for fermentation CO_2 purification.

HYDROGEN

USES AND ECONOMICS. Hydrogen has long been an important *gaseous* raw material for the chemical and petroleum industries. The annual production of merchant hydrogen is in excess of 3×10^9 m^3 and is only a very small part of the total industrial production. Table 4.2 gives the hydrogen requirements for making some typical chemicals. Hydrogen is sold as gas and liquid. Liquid hydrogen is the most profitable, is produced by only three companies, and is shipped by tank car, truck, or barge. Gaseous hydrogen is made by many companies and is shipped in "tube trailers" holding about 4300 m^3.[7] The use of *metal hydrides* as *hydrogen*

[7]Key Chemicals—Hydrogen, *Chem. Eng. News* 59 (30) 19 (1981); The Changing Economics of Hydrogen, *Chem. Week*, 131 (24) 42 (1982); Snape and Lynch, Metal Hydrides Make Hydrogen Accessible, *CHEMTECH* 10 (9) 578 (1980); 10 (12) 768 (1980); Kelley, Escher, and van Deelen, Hydrogen Uses and Demands through 2025, *Chem. Eng. Prog.* 78 (1) 58 (1982); Hydrogen Economy Still in the Future, *Chem. Eng.* 89 (15) 17 (1982).

***Table* 4.2** Hydrogen Required for Typical Products

Raw Material to Be Hydrogenated	Product	Hydrogen Required at 150°C, m^3
Phenol	Cyclohexanol	787
Nitrogen	Ammonia	2645
Naphthalene	Tetralin	378
Olein	Stearin	82
Diisobutylene	Isooctane	1600
Carbon monoxide	Methanol	1715

SOURCE: Stengel and Shreve, Economic Aspects of Hydrogenation. *Ind. Eng. Chem.* 32 1212 (1940). All hydrogen requirements are per metric ton of product, except synthetic methanol and isooctane are per cubic meter.

sponges is increasing for storing hydrogen compactly at moderate pressure, that is 2 MPa, compared with 14 MPa of the common compressed hydrogen cylinder. The hydrides used are alloys of magnesium-nickel, iron-titanium, lanthanum-nickel, and misch metal–nickel.[8]

HYDROGEN MANUFACTURE. Hydrogen is derived almost exclusively from carbonaceous materials, primarily hydrocarbons, and/or water. These materials are decomposed by the application of energy, which may be electrical, chemical, or thermal. Examples include electrolysis of water, steam reforming of hydrocarbons, and thermal dissociation of natural gas (Chap. 5). Hydrogen is also produced by partial oxidation of hydrocarbons and by such less important methods as the steam-iron process, water-gas and producer-gas processes, and separation from coke-oven[9] gas and refinery off-gas streams. Diffusion through a palladium-silver alloy furnishes very high purity hydrogen.

Electrolytic Method.[10] The electrolytic process produces high-purity hydrogen and consists of passing direct current through an aqueous solution of alkali, and decomposing the water according to the following equation:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \qquad \Delta H = +569 \text{ kJ}$$

The theoretical decomposition voltage for this electrolysis is 1.23 V at room temperature; however, because of the overvoltage of hydrogen on the electrodes and also cell resistance itself, voltages of 2.0 to 2.25 V are usually required. A typical commercial cell electrolyzes a 15% NaOH solution, uses an iron cathode and a nickel-plated-iron anode, has an asbestos diaphragm separating the electrode compartments, and operates at temperatures from 60 to 70°C. The nickel plating of the anode reduces the oxygen overvoltage. Most types of cells produce about 56 L (74.5 L, theoretically) of hydrogen and half as much oxygen per megajoule. The gas is about 99.7% pure and is suitable even for hydrogenating edible oils. The cells are of two types: the bipolar, or filter-press, type, where each plate is an individual cell, and the unipolar, or tank, type, usually containing two anode compartments with a cathode compartment between them. The unipolar cells may be open or closed tanks. In most installations the oxygen produced is wasted unless it can be used locally. Hydrogen is also obtained from other electrolytic processes, for example, electrolysis of salt brine (cf. Chaps. 10 and 11).

Steam-Hydrocarbon Reforming Process. This process consists of catalytically reacting a mixture of steam and hydrocarbons at an elevated temperature to form a mixture of H_2 and oxides of carbon. The following basic reactions occur:

$$C_nH_m + nH_2O = nCO + \left(\frac{m}{2} + n\right)H_2$$

$$CO + H_2O = CO_2 + H_2$$

[8]Misch metal is a mixture of crude rare-earth metals.

[9]New Nitrogen Plant, Geneva Works, Hydrogen Extracted from 252 Coke Ovens, *U S Steel Quart.* **11** (3) 1 (1957); U S Steel to Increase Chemicals Capacity, Hydrogen, etc., *Chem. Eng. News* **41** (41) 25 (1964).

[10]Pressure Lowers Electrolytic H_2 Cost, *Chem. Eng.* **67** (5) 60 (1960) (cell is operated at 3 MPa); Solid Electrolytes Offer Route to Hydrogen, *Chem. Eng. News* **51** (35) 15 (1973); *Chem. Eng.* **89** (7) 25 (1982).

Although the equations are shown for the general case of any hydrocarbon feed, only light hydrocarbons have been successfully used in commercial practice. Natural gas is most common, and propane and butane (LPG) are also frequently used. With the use of a specially prepared catalyst, naphtha is also a suitable feedstock.

The first reaction is the reforming reaction. It is highly endothermic, and the moles of product exceed the moles of reactant so the reaction goes to completion at high temperature and low pressure. Excess steam is normally used. Although the basic purpose is to prevent carbon formation, it also helps force the reaction to completion.

The second reaction is the water-gas-shift reaction. It is mildly exothermic and is favored by low temperature but unaffected by pressure. Excess steam also forces this reaction to completion and is so used. A catalyst is usually employed. Both these reactions occur together in the steam-reforming furnace at temperatures of 760 to 980°C. The composition of the product steam depends upon the process conditions, including temperature, pressure, and excess steam, which determine equilibrium, and the velocity through the catalyst bed, which determines the approach to equilibrium. A typical product contains approximately 75% H_2, 8% CO, and 15% CO_2; the remainder consists of nitrogen and unconverted methane.

For the production of additional H_2, the reformer is followed by a separate stage of water-gas-shift conversion. Additional steam is added, and the temperature is reduced to 315 to 370°C to obtain more favorable equilibrium conditions. A single stage converts 80 to 95% of the residual CO to CO_2 and H_2. Because the reaction is exothermic, the reactor temperature rises; this enhances the reaction rate but has an adverse effect on the equilibrium. When high concentrations of CO exist in the feed, the shift conversion is usually conducted in two or more stages, with interstage cooling to prevent an excessive temperature rise. The first stage may operate at higher temperatures to obtain high reaction rates, and the second at lower temperatures to obtain good conversion.

The process using propane is shown in Fig. 4.3, and the material requirements are listed in Table 4.3. This process[11] can be broken down into the following coordinated sequences:

Propane is vaporized by steam.

Propane vapor is desulfurized by contact with activated carbon to prevent deactivation of the catalyst.

Propane vapor mixed with steam is reformed (Fig. 4.4) over a nickel catalyst at about 815°C in alloy tubes in a combustion furnace (to furnish the heat for this endothermic reaction).

The gases H_2, CO, and some CO_2 are cooled to about 370°C, and the partial pressure of water increased by addition of steam or condensate, and passed over an iron oxide catalyst in the first-stage CO converter, where 90 to 95 percent of the CO is converted to CO_2 with more H_2. (This is the so-called shift,[12] or water-gas-conversion, reaction.)

These hot gases are first cooled by heat exchange with the gases leaving the first-stage CO_2 absorber before entering the second-stage CO converter, and finally by water to about 38°C.

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[11]Further details and other flowcharts as well as technical pamphlets on hydrogen should also be consulted. These are available from Girdler Corp., Louisville, Ky., Chemical Construction Co., New York, N.Y., and M. W. Kellogg Co., Houston, Texas; see also van Weenan and Tielrooy, Optimizing Hydrogen Plant Design, *Chem. Eng. Prog.* 83 (2) 37 (1983).

[12]Moe, Design of Water-gas Shift Reactors, *Chem. Eng. Prog.* 58 (3) 33 (1962). Rate equations for producing hydrogen.

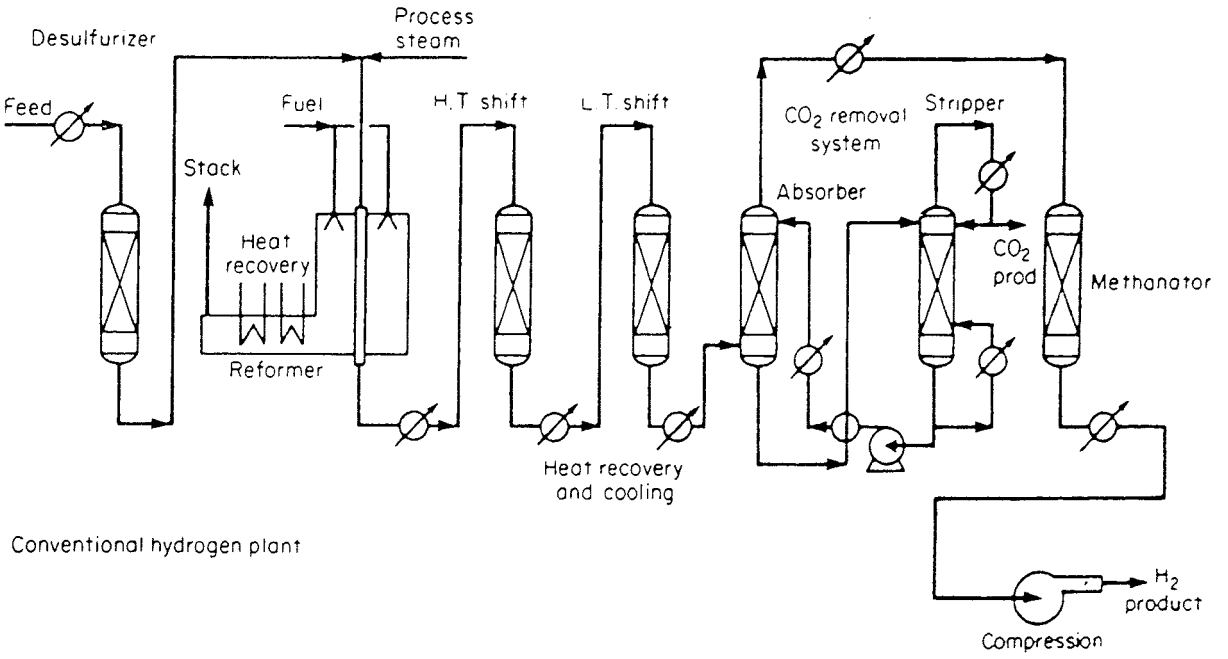

Fig. 4.3. Simplified hydrogen production processing train. *(Union Carbide Corp., Linde Div.)*

The cooled gases are scrubbed with a monoethanolamine solution in the first-stage Girbotol absorber to remove essentially all the CO_2. Following this, the gases heated by exchange with the gases leaving the first-stage CO converter are passed through the second-stage CO converter, also followed by second-stage CO_2 absorber.

The gases low in CO_2 and CO are heated to about 315°C by exchange with gases from the second-stage CO converter and passed to the methanator over a nickel catalyst to convert essentially all the carbon oxides to methane by reaction with H_2.

The product H_2 gas from the methanator is cooled to 38°C (with water), leaving it pure except for saturation with water vapor. The lean amine solution from the Girbotol reactivator is first pumped through the second-stage CO_2 absorber to reduce the CO_2 content of the H_2 gas to a minimum and then pumped to the first-stage CO_2 absorber to remove the bulk of the CO_2 in the H_2 gas. The rich solution is returned to the reactivator through heat exchangers, and the CO_2 is stripped out by steam.

The CO_2, about 55 kg/100 m^3 H_2, can be recovered for sale or use.

Catalysts. In many reactions connected with hydrogen manufacture, various catalysts are necessary, for example, nickel for steam-hydrocarbon reforming, iron oxide for CO conversion or the shift reaction, nickel for methanation, and nickel for ammonia cracking or dissociation.

Partial Oxidation Processes. These rank next to steam-hydrocarbon processes in the amount of hydrogen made. They can use natural gas, refinery gas, or other hydrocarbon gas mixtures as feedstocks, but their chief advantage is that they can also accept liquid hydrocarbon feedstocks such as gas oil, diesel oil, and even heavy fuel oil. There are three commercial versions of the process. It was originally developed by Texaco, and variations were

***Table* 4.3** Product Analysis and Utility Requirements for Hydrogen Production by Steam Hydrocarbon Process*

Product Analysis, Vol. %	Low-Pressure Reforming, Vol. %	Pressure Reforming, Vol. %
Carbon monoxide	0.001	0.001
Carbon dioxide	0.001	0.001
Methane	0.400	1.200
Hydrogen (minimum)	99.598	98.798
Raw Material and Utility Requirements, per 100 m^3 of hydrogen		
Process material		
Propane, sulfur free, L	36	37
Natural gas, 37 MJ/m^3, m^3	25	25.3
Fuel, natural gas, propane, or oil, MJ	795	850
Steam, 480 kPa		
Propane for process, kg	445	238
Natural gas for process, kg	330	214
Cooling water, 17°C rise		
Propane for process, L	17,900	11,260
Natural gas for process, L	15,900	10,600
Power, exclusive of lighting, MJ	6.3	7.6

*The purification includes two stages of carbon monoxide conversion and carbon dioxide removal and one stage of methanation.

introduced later by both Shell and Montecatini,[13] which differ primarily in the design and operation of the partial oxidation burner. All employ noncatalytic partial combustion of the hydrocarbon feed with oxygen in the presence of steam in a combustion chamber at flame temperatures between 1300 and 1500°C. When methane is the principal component of the feedstock, the reactions involved are:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H = +802 \text{ kJ}$$
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = -206 \text{ kJ}$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = -247 \text{ kJ}$$

The first reaction is highly exothermic and produces enough heat to sustain the other two reactions, which are endothermic. The net reaction is as follows:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2$$

This reaction is exothermic, and so the overall process is a net producer of heat; for efficient operation, heat recovery (using waste heat boilers) is important.

The product gas has a composition that depends upon the carbon/hydrogen ratio in the feed and the amount of steam added. Pressure does not have a significant effect on compo-

[13]ECT, 3d ed., vol. 12, pp. 939–982, 1980; Hydrogen Manufacture, *Hydrocarbon Process.* 58 (4) 168 (1979); The Search for Cheaper Hydrogen, *Chem. Week* 130 (9) 42 (1982); Hydro-

sition, and the process is usually conducted at 2 to 4 MPa, permitting the use of more compact equipment and reducing compression costs. The following composition is typical for a fuel oil feedstock:

	Mole Percent
H_2	48.0
CO	46.1
CO_2	4.3
CH_4	0.4
N_2, etc.	0.3
H_2S	0.9
	100.0

This gas has a much higher carbon oxides/hydrogen ratio than steam reformer gas.

In the commercial application of the Texaco process, preheated oil is mixed, under pressure, with oxygen and preheated steam and fed to the partial oxidation burner. About 26 m^3 of 95 to 99% oxygen is used per 100 m^3 of H_2 + CO produced. The product gas is cooled by a direct-contact water quench followed by a water scrubber and a filter, all of which serve to remove unreacted carbon from the product gas. The carbon is removed from the quench water, for example, by filtering, for disposal or reuse, or it may be discarded as a water slurry.

The remaining process steps for conversion of the partial oxidation product gas to hydrogen are the same as for the steam-hydrocarbon reforming process: water-gas-shift conversion, CO_2 removal via monoethanolamine scrubbing, and methanation.

Coal Gasification Processes. Coal as a source of hydrogen will assume increasing importance in the future as reserves of gaseous and liquid hydrocarbon feedstocks decrease. Although coal was used in early water-gas and producer-gas plants for the manufacture of a H_2–CO mixture, these plants cannot compete with more modern processes. The various processes have been described in Chap. 6. The gases produced require the water-gas-shift conversion and subsequent purification to produce high-purity hydrogen. Table 4.4 shows a comparison of the four main processes for the production of hydrogen.

Cracked Ammonia. A mixture of nitrogen, 1 volume, and hydrogen, 3 volumes, may be prepared from the cracking or dissociation of ammonia. This mixed gas can be used for hydrogenation because the nitrogen is inert. The process consists of vaporizing the liquid ammonia from cylinders, heating it to 870°C, passing it over an active catalyst, and then cooling it in heat exchangers where the incoming gas may be vaporized. A single 68-kg cylinder of anhydrous ammonia will produce 190 m^3 of cracked ammonia. This is equivalent to the contents of about 33 hydrogen cylinders.

HYDROGEN PURIFICATION

Carbon Monoxide Removal. High concentrations of carbon monoxide are commonly reduced by conversion to hydrogen via the water-gas-shift reaction; see Fig. 4.3. Removal by scrubbing in solutions of complex copper ammonium salts has been used commercially.

Carbon Dioxide and Hydrogen Sulfide Removal. Many processes for the removal of acid gases have been employed commercially.[14]

[14]Strelzoff, Choosing the Optimum CO_2-Removal System, *Chem. Eng.* 82 (19) 115 (1975).

Table 7.4 Comparison of Hydrogen Production Alternatives

	Steam Reforming	Coal Gasification	Electrolysis	Thermochemical Decomposition
Appropriate overall thermal efficiency, %	70	60–65	32 (SPE)* 21–25 (KOH)	Upper limit 55
State of the art	Well-known technology	Mature technology available	Proven, reliable technology	Research stages
Environmental effects	Depletion of natural gas and other light hydrocarbons	Impacts of coal mining; air pollution likely to be less than via electricity from coal	Pollution problems with electricity generation	High efficiency means less resource use. Possible release of harmful chemicals
Advantages	Currently the cheapest method in the U.S	Cheapest and most secure near-term alternative to methane reforming;	Small plant size; can use nonfossil fuel	Can use nonfossil fuel
Disadvantages	Scant long-term potential due to limitations on methane supply	Ultimate limitation is exhaustion of coal resources; requires large plant size	High cost, low net energy efficiency	Materials problems in reactant containment; large complex plant
Estimated hydrogen production costs,* $/GJ product (1980 $)	7.17	10.02	21.05	

*Solid Polymer Electrolyte (General Electric).

SOURCE: *Chem. Eng.* 87 (14) 80 (1980).

1. *Monoethanolamine (MEA) or Girbotol process.* A water solution of MEA is reacted with CO_2 in an absorber vessel under pressure at room temperature. The MEA solution is then heated and fed to a reactivation column where the MEA · CO_2 complex is dissociated by stripping with steam at 90 to 120°C and near atmospheric pressure. The CO_2 and steam leave at the top of the reactivation column, and the regenerated solution leaves at the bottom, is cooled, and is pumped back to the absorber. The chemical reactions involved are:

$$2NH_2CH_2CH_2OH + CO_2 + H_2O = (HOCH_2CH_2NH_3)_2CO_3$$
$$NH_2CH_2CH_2OH + CO_2 + H_2O = HOCH_2NH_3HCO_3$$

Contrasted with physical absorption types of CO_2-removal processes, the MEA process is capable of reducing the CO_2 concentration in the process gas to less than 0.01% by volume.

A major problem associated with the use of MEA solutions is their corrosive effect on process equipment. Corrosion is most severe at elevated temperatures and where the acid gas concentration in solution is the highest. Control of corrosion is achieved by using stainless steel at potential trouble spots, by limiting the concentration of MEA in aqueous solution in order to limit the CO_2 in solution, by excluding oxygen from the system, and by removing oxidation and degradation products using side-stream distillation. Another system uses a corrosion inhibitor (amine guard),[15] which has greatly decreased corrosion as an operating problem even with increased CO_2 loadings.

2. *Hot potassium carbonate process.* This process, developed originally by the Bureau of Mines, is particularly useful for removing large quantities of CO_2. Although it can remove CO_2 down to 0.1% by volume in the gas being purified, it is generally more economical at purity levels of 1% or greater. By absorbing CO_2 under pressure in hot solution close to its boiling point and regenerating it at the same temperature but at near-atmospheric pressure, steam consumption is reduced and heat exchangers are eliminated. Process improvements have been obtained through the use of catalytic additions and promoters to the solution, such as in the Giammarco-Vetrocoke[16] and the Catacarb processes.[17]

3. *Physical solvent processes.*[18] These are processes in which CO_2 is removed by physical solution in a solvent, which is often proprietary. Examples of this class of process are the Rectisol process using cold (approximately −60°C) methanol, the Fluor solvent process using a nonaqueous organic solvent such as propylene carbonate, the Sulfinol process using an organic solvent, sulfolane (tetrahydrothiophene dioxide), the Selexol process using the dimethyl ether of polyethylene glycol, and the Purisol process using *N*-methyl-2-pyrrolidone. Aqueous ammonia solutions have been used for removal of CO_2 and H_2S, particularly in ammonia synthesis plants where ammonia is available. Water has also been used, but CO_2 solubility is poor, requiring high-pressure operation, and hydrogen losses, because of solubility, are high.

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[15]Butwell, Hawkes and Mago, Corrosion Control in CO_2 Removal Systems, *Chem. Eng. Prog.* **69** (2) 57 (1973); Kubek and Butwell, "Amine Guard Systems in Hydrogen Production," paper presented at AIChE meeting, April 1–15, 1979, at Houston, Texas.

[16]*Chem. Eng.* **67** (19) 166 (1960) (flowchart)

[17]Eickmeyer, Catalytic Removal of CO_2 (Hot Carbonates), *Chem. Eng. Prog.* **58** (4) 89 (1962).

[18]Physical Solvent Stars in Gas Treatment/Purification (Selexol) *Chem. Eng.* **66** (13) 54 (1970).

Adsorptive Purification. Fixed-bed adsorption can remove such impurities as CO_2, H_2O, CH_4, C_2H_6, CO, Ar, and N_2, among others. One type of process is the thermal-swing process in which the impurity is adsorbed at a low temperature and desorbed thermally by raising the temperature and passing a nonadsorbable purge gas through the bed to aid desorption and carry the desorbed gas from the bed. For continuous operation two beds are necessary; while one bed is onstream, the second bed is being regenerated.

A second type of process is the pressure-swing adsorption process (PSA) in which the impurities are adsorbed by a molecular sieve under pressure and desorbed at the same temperature but at a lower pressure. A purge gas may be used. For continuous operation, at least two beds are required. Its principal advantage is that it can operate on a shorter cycle than the thermal-swing process, thereby reducing vessel sizes and adsorbent requirements. It is capable of purifying a typical crude hydrogen stream to a high-purity hydrogen product containing 1 to 2 ppm total impurities.

Integration of PSA technology into the steam-reforming process allows more than the removal of all the impurities[19] from the hydrogen gas. In the conventional reformer the steam-to-carbon ratio is set to avoid carbon formation in the tubes, to provide enough steam for the low-temperature shift converter, and to provide a heat balance in the scrubbing section. With PSA the only constraint for the reformer designer is to provide a high enough steam-to-carbon ratio to avoid carbon deposition. This often allows a ratio as low as 3:1 compared with 5 to 6:1 in the scrubbing process.

Cryogenic Liquid Purification. An impure hydrogen stream can be partially purified by simply cooling to the appropriate cryogenic temperature,[20] where the impurities will condense and can then be separated as a liquid stream. This is often used for bulk removal of light hydrocarbons from hydrogen in a refinery off-gas. The product purity obtainable depends upon the vapor pressure of the impurity, and high purities are not readily attainable in most cases.

For additional purification, Linde removes low-boiling contaminants in a hydrogen gas stream at 2.1 MPa and $-180°C$ by washing successively with liquid methane (to remove N_2 and CO) and liquid propane (to remove CH_4) to give 99.99% hydrogen. Final purification employs activated carbon, silica gel, or molecular sieves. Low temperatures for washing with liquid nitrogen or for fractionation are also used to remove impurities.

The parahydrogen content of bulk liquid hydrogen should be greater than 95%. The terms ortho and para refer to the direction of nuclear spin in the hydrogen molecule. Hydrogen normally contains 25% para at room temperature but slowly converts to nearly pure para at liquid temperature. During liquefaction, hydrogen should be catalytically[21] converted from

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[19]Large Quantities of High Purity Hydrogen, *Chem. Eng.* 86 (23) 90 (1979); Corr, Dropp, and Rudelstorfer, PSA Produces Low Cost High Purity H_2, *Hydrocarbon Process.* 58 (3) 119 (1979); Simple Gas Adsorber Features Self-Regeneration, *Chem. Eng.* 88 (24) 71 (1981); Kaplan, Metal Hydrides Selectively Remove H_2 from Gas Streams, *Chem. Eng.* 89 (16) 34 (1982).

[20]Haslain, Which Cycle for H_2 Recovery?, *Hydrocarbon Process.* 51 (3) 101 (1972); Lehman and VanBaush, Cryogenic Purification of Hydrogen, *Chem. Eng. Prog.* 80 (1) 44 (1976).

[21]Schmauch and Singleton, Technical Aspects of Ortho-Para Hydrogen Conversion, *Ind. Eng. Chem.* 56 (5) 20 (1964); Schmauch et al., Activity Data on Improved Para-Ortho Conversion Catalysts, *Chem. Eng. Prog.* 59 (8) 55 (1963); Lipman, Cheung, and Roberts, Continuous Conversion Hydrogen Liquefaction, *Chem. Eng. Prog.* 59 (8) 49 (1963).

the ortho to the para form to prevent subsequent exothermic conversion and evaporation of the product in storage. The heat of conversion (703 J) is great enough, compared with the heat of vaporization (444 J), to cause considerable loss.

An interesting development is the use of semipermeable membranes either to produce pure hydrogen or to adjust the gas stream composition. Hollow fibers of polysulfone covered with a proprietary coating (Monsanto's Prism system) are used for the membranes. The separator consists of a bundle of fibers (10,000 to 100,000) oriented vertically that is capped at one end and placed on an open epoxy tube sheet on the other. The fibers are 800 μm in diameter or less and the whole vessel is 10 or 20 cm in diameter by 3 m long. The separation of the components of the entering gas is determined by the rates at which the substances permeate the membrane. The modules can be run in series or parallel to attain high purities or to vary the composition of synthesis gas. One application is the production of 1.3/1 H_2/CO gas for oxo alcohol manufacture from 3.1/1 H_2/CO gas.[22]

OXYGEN AND NITROGEN

USES AND ECONOMICS. In 1981 the production of oxygen in the United States was 11.75×10^9 m^3. This represented a drop from 1979 and 1980, and for the second year in a row nitrogen production exceeded that of oxygen.[23]

Oxygen is produced by the liquefaction and rectification of air in highly efficient, well-insulated, compact plants or by the pressure-swing adsorption system. Supply of raw material is not a problem and, because transportation of the product adds considerably to the cost, plants are usually located close to the point of consumption.[24] An air separation plant may be located on the customer's property and, as such, is known as an on-site plant. It may be owned and operated off site by the designer and builder of the plant and the product delivered by a short pipeline. At some air separation complexes, several customers are serviced by a single pipeline many kilometers in length. In such cases, oxygen assumes many of the characteristics of a utility.

Air separation plants vary in size from small cryogenic units producing less than 1 t/day to giant plants producing more than 1800 t/day (Fig. 4.4). PSA plants operate in the size range of 13 kg to 27 t/day. The bulk of the oxygen is produced at high purity (99.5%). Low purity usually refers to the 95 to 99% purity range. For high-purity oxygen, the impurities are argon and traces of rare gases, hydrocarbons, and carbon dioxide.

A major use of oxygen is[25] the production of steel in open-hearth or basic oxygen furnaces. The steel industry also uses oxygen for removal of scale from billets by an oxyacetylene flame and in oxygen lances for cutting out imperfections. The chemical industry[26] is a large con-

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[22]MacLean and Graham, Hollow Fibers Recover Hydrogen, *Chem. Eng.* 87 (4) 54 (1980) Unique Membrane System Spurs Gas Separation, *Chem. Eng.* 88 (24) 62 (1981).

[23]Key Chemicals, Oxygen, *Chem. Eng. News* 60 (29) 21 (1982).

[24] ECT, 3d ed., vol. 16, 1981, p. 653; vol. 15, 1981, p. 932.

[25]Wolff, Eyre, and Grenier, Oxygen Plants: 10 Years of Development and Operation, *Chem. Eng. Prog.* 75 (7) 83 (1979).

[26]Gans, Choosing Between Air and Oxygen for Chemical Processes, *Chem. Eng. Prog.* 75 (1) 67 (1979).

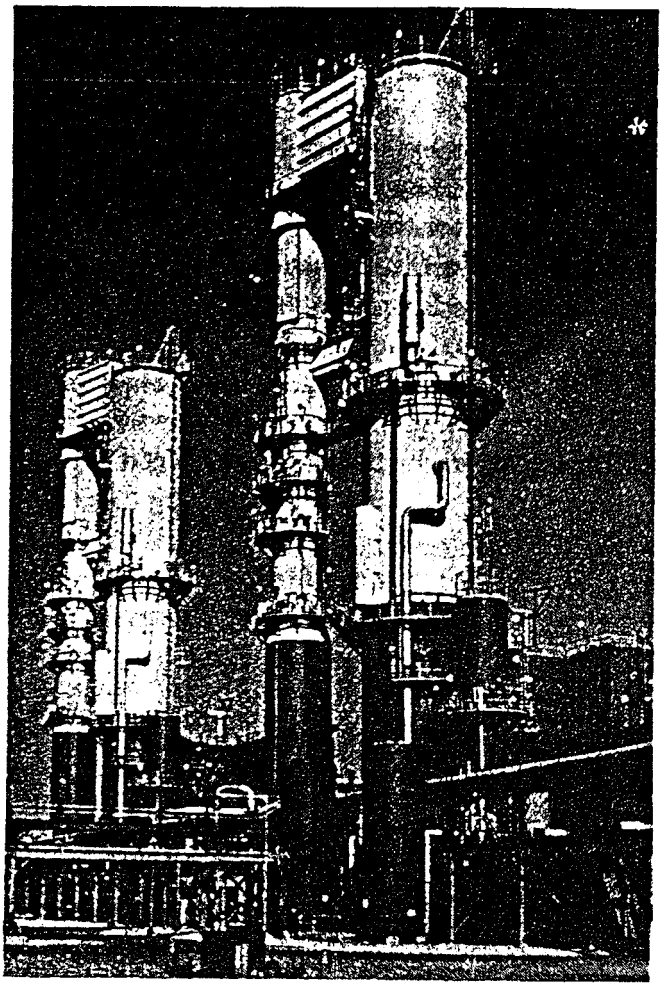

Fig. 4.4. Cryogenic oxygen plant producing 1800 t/day at Burns Harbor, Ind. *(Union Carbide Corp., Linde Div.)*

sumer of oxygen, using it in such applications as acetylene and ethylene oxide production and in ammonia and methanol production via partial oxidation of hydrocarbons.

Other uses include metalworking applications, underground gasification and fireflooding, enhancement of combustion processes in nonferrous metallurgical processes, medical purposes in hospitals, and aviators' breathing oxygen. In an aerospace application, the first stage of the Saturn V rocket required 1.5×10^6 kg of liquid oxygen for fuel oxidation. Consumption for this purpose by NASA peaked in the mid-1960s at about 280×10^6 m^3/year and has since declined with the completion of the Apollo program. The greatest new potential use for oxygen is in synthetic fuels production: coal gasification and coal liquefaction. It is predicted that by 1990 the amount used for this could surpass that used for steel.

Environmental and energy problems are producing new applications for oxygen. Municipalities as well as industry are now aerating wastewater streams with oxygen instead of air in the activated sludge process for secondary treatment.[27] Oxygen is also used for the disposal and conversion of refuse to usable by-products.

Nitrogen became the largest-volume industrial gas in 1981 with the production of 13.6×10^9 m^3.[28] The major use of nitrogen is as a gaseous blanket that excludes oxygen and moisture.

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[27]Direct Oxygenation of Wastewater, *Chem. Eng.* 78 (27) 66 (1971); see Chap. 3.

[28]Key Chemicals, Nitrogen, *Chem. Eng. News* 60 (29) 22 (1982); Schell, A Buoyant Industrial Gas Industry Faces the Future, *Chem. Business* May 4, p. 18, 1981. The Air-Gas Merchant Market Heats Up, *Chem. Week* 132 (5) 49 (1983).

***Table* 4.5** Properties of Air and Constant Constituents

Gas	Volume %	Triple Point, K	Boiling Point, K	Critical Temp., K	Critical Pressure, MPa
Nitrogen	78.084	63.156	77.35	128.2	3.39
Oxygen	20.946	54.363	90.19	154.58	5.04
Argon	0.934	83.78	87.27	150.8	4.81
Hydrogen	0.00005	13.96	20.27	33.19	1.29
Neon	0.001921	24.55	27.09	33.19	2.68
Helium	0.0005239	*	4.215	5.20	0.22
Krypton	0.0001139	115.95	119.81	209.4	5.40
Xenon	0.0000087	161.3	165.04	289.8	5.74
Carbon dioxide	0.02–0.04	216.6	194.68†	304.2	7.25

*Has no triple point.

†Sublimation temperature.

SOURCE: Scott, *Cryogenic Engineering*, Van Nostrand, New York, 1962, pp. 268–321; Mirtov, *Gaseous Composition of the Atmosphere and Its Analyses*, transl. NASA TTF-145, OTS 64-11023, U.S. Dept. Commerce, 1964.

For this, it must be dry and have an extremely low oxygen content (less than 10 ppm). The other use is for obtaining extremely low temperatures, down to −210°C. The largest consumption of nitrogen is in the manufacture of ammonia. Production statistics usually do not include this usage because the nitrogen usually originates from feedstock and air rather than from merchant nitrogen. Other uses by the chemical industry are in applications to exclude oxygen or moisture, such as blanketing of polymerization processes, or for applications as a diluent, for example, in the control of reaction rates. It is replacing traditional blanketing agents, such as natural gas, in the manufacture of electronic products.

It is extensively used by the steel industry for blanketing and bright-annealing. The food processing industry uses nitrogen for food freezing and as a refrigerant in the processing and refrigerated transport of frozen foods. Other uses for liquid nitrogen include low-temperature metal treatment, shrink-fitting of parts, deflashing of molded plastic and rubber parts, and in cryobiology for storage of biological materials such as whole blood and bull semen, and as a refrigerant in cryosurgical procedures.

A new, rapidly growing use of nitrogen is for tertiary oil recovery in old oil fields. The gas is used to maintain pressure in the wells. This was formerly done with natural gas. It is usual to use merchant nitrogen for this purpose until it proves to be satisfactory. When it is, an on-site producing plant is constructed.

MANUFACTURE. Oxygen and nitrogen are produced principally by the liquefaction and rectification of air.[29] Production by the electrolytic dissociation of water is of little significance. Air is a mixture of many substances, of which eight are found in unvarying concentration; seven of these are of commercial importance. Table 4.5 lists the major constituents of air and their properties.

The production of high-purity gaseous oxygen from air via the cryogenic process is illustrated by the flowsheet in Fig. 4.5. Filtered air is compressed to approximately 520 kPa in a centrifugal compressor and aftercooled. After separating out any liquid water, the air enters the reversing heat exchanger and is cooled to near its dew point in countercurrent heat

[29]Latimer, Distillation of Air, *Chem. Eng. Prog.* 63 (2) 35 (1967) (extensive treatment of air separation technology); Advances in Large Scale Oxygen Production, *Adv. Pet. Chem. Refin.*, vol. 9, chap. 1, Interscience, New York, 1964.

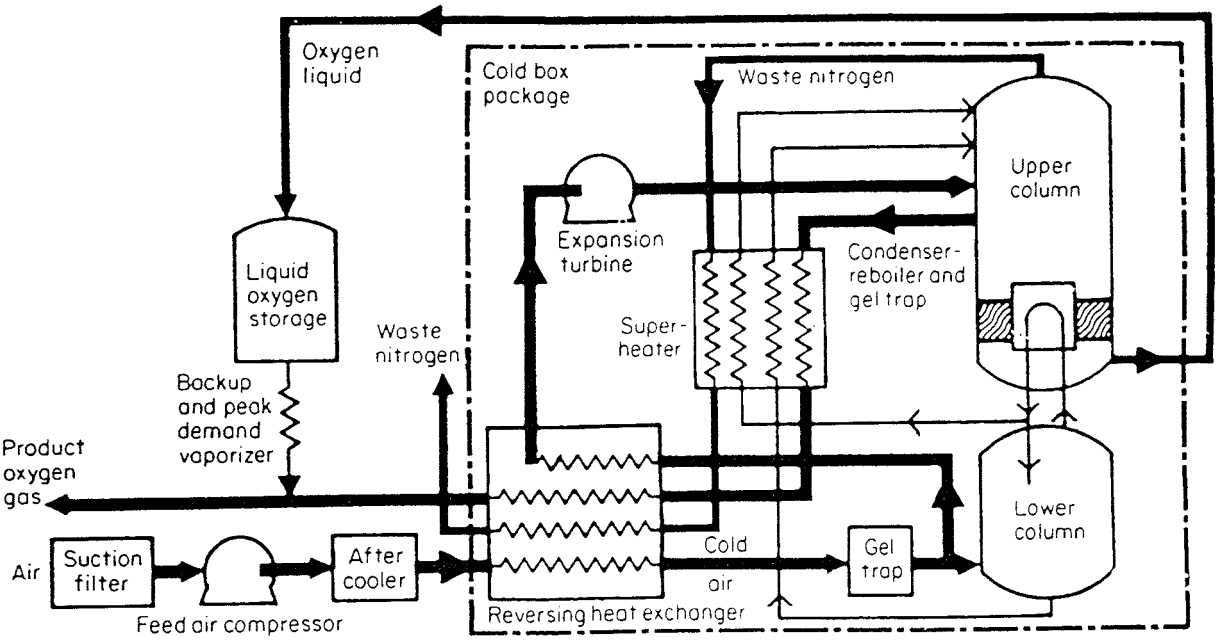

Fig. 4.5. Flowchart for on-site air separation unit. *(Union Carbide Corp., Linde Div.)*

exchange with the outgoing gaseous products. As the air cools, moisture is first condensed and frozen on the walls of the heat exchanger passage. At lower temperatures carbon dioxide freezes and is also deposited on the heat exchanger passage walls. The air emerging from the reversing heat exchanger is completely dry and has had over 99% of the carbon dioxide removed. Gas-phase, fixed-bed adsorption is used to remove the remaining carbon dioxide and, more importantly, any hydrocarbons entering with the air which would be hazardous in the presence of liquid oxygen. The cleaned air is then fed to the bottom tray of the lower column of the double-column rectifier. This is shown in more detail in Fig. 4.6.

The double-column rectifier consists of two tray-type distillation columns which are thermally connected at the center through a heat exchanger, which serves as a condenser for the lower column and a reboiler for the upper. Because nitrogen is more volatile than oxygen, it will ascend each column and oxygen will descend. Thus, on the reboiler side of the upper column, there is a pool of high-purity, boiling, liquid oxygen, while on the condenser side of the lower column, nearly pure nitrogen is being condensed. Because the normal boiling point of oxygen is 12.8°C higher than that of nitrogen, the pressure in the lower column must be high enough to raise the condensing temperature of nitrogen sufficiently to provide a positive temperature-driving force in the main condenser. The condensed nitrogen is split as it leaves the main condenser; one portion returns to the lower column as reflux, and the other is diverted to the upper column, through the nitrogen superheater, also for use as reflux. An oxygen-rich (35%) liquid stream leaves the bottom of the lower column and, after being subcooled in the nitrogen superheater, serves as the main feed stream for the upper column. The two liquid streams entering the upper column are first subcooled to reduce flashing when throttled to the lower pressure of the upper column. The oxygen product is removed as saturated vapor from the main condenser, and a high-purity nitrogen product is removed as saturated vapor from the top of the upper column. The remaining gas is removed as a low-purity waste nitrogen stream several trays from the top of the upper column.

Carbon dioxide and light hydrocarbons tend to accumulate in the liquid oxygen in the main condenser. These constituents are removed by recirculating the main condenser liquid through a silica gel adsorption trap to prevent the buildup of carbon dioxide and hazardous hydrocarbons.

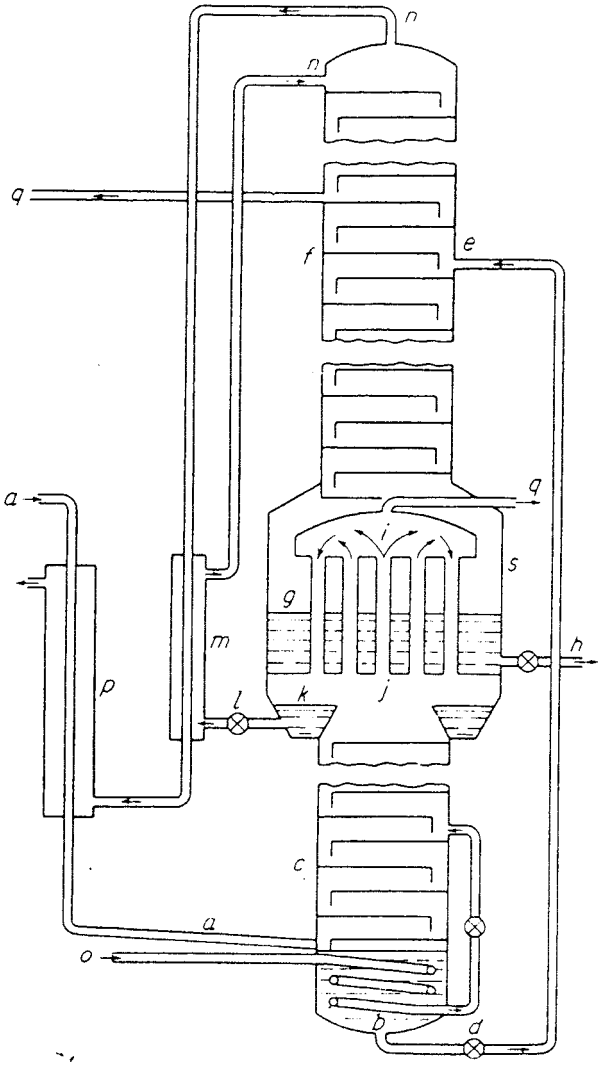

Fig. 4.6. Diagram of Linde double column and main condenser. The rectifier separates liquid air into the more volatile nitrogen (bp 77.4 K) and the less volatile oxygen (bp 90.2 K). (*a*) cold-air feed at 582 to 651 kPa; (*b*) kettle liquid rich in oxygen (about 35% O_2); (*c*) lower or high-pressure column (582 to 651 kPa); (*d*) throttling valve for kettle liquid; (*e*) liquid feed to upper column; (*f*) upper or low-pressure column (122 to 183 kPa); (*g*) accumulated oxygen liquid; (*h*) exit for product oxygen, 99.5% pure; (*i*) plate-and-fin main condenser-reboiler; (*j*) liquid nitrogen reflux to lower column; (*k*) liquid nitrogen reflux to upper column; (*l*) throttling valve for nitrogen reflux; (*m*) plate-and-fin heat exchanger, liquid-nitrogen reflux and kettle liquid to product nitrogen and waste nitrogen; (*n*) cold nitrogen vapor to main condenser, (*o*) cold exhaust air from expansion turbine; (*p*) cold product nitrogen gas; (*q*) cold waste nitrogen. (*Union Carbide Corp., Linde Div.*)

The two nitrogen and the oxygen streams are superheated to approximately 100 K in their respective superheaters and are delivered to the reversing heat exchangers for warm-up to the ambient temperature in heat exchange with the incoming air. The high-purity nitrogen and high-purity oxygen are warmed in separate nonreversing passages, while the waste nitrogen flows through passages which periodically reverse with the air passages. The waste nitrogen thus flows past the solid carbon dioxide and frozen moisture previously deposited from the air and causes the deposits to sublime into the waste nitrogen and to be carried out of the heat exchanger. Periodic reversal of the air and waste nitrogen passages ensures that the heat exchanger is maintained in a clean, operable condition.

Refrigeration to overcome heat influx to the process is provided by expanding a portion of the air stream through a centrifugal expansion turbine. Ideally, this is an isentropic process which reduces the enthalpy of the air being expanded and rejects the energy from the process via the turbine shaft. Usable work can be recovered by coupling an electric generator, for example, to the turbine shaft. Clean, cold air for the turbine is withdrawn downstream of the absorber and reheated in a separate passage of the reversing heat exchanger to the proper temperature for introduction to the turbine. The reheating also serves to control the temperature pattern to help maintain clean operation of the reversing heat exchanger. Air exhausting from the turbine is fed to the proper tray of the upper column.

Heat exchangers are usually of the very compact brazed aluminum plate-and-fin construction. Distillation trays may be either perforated or bubble cap. Materials of construction are

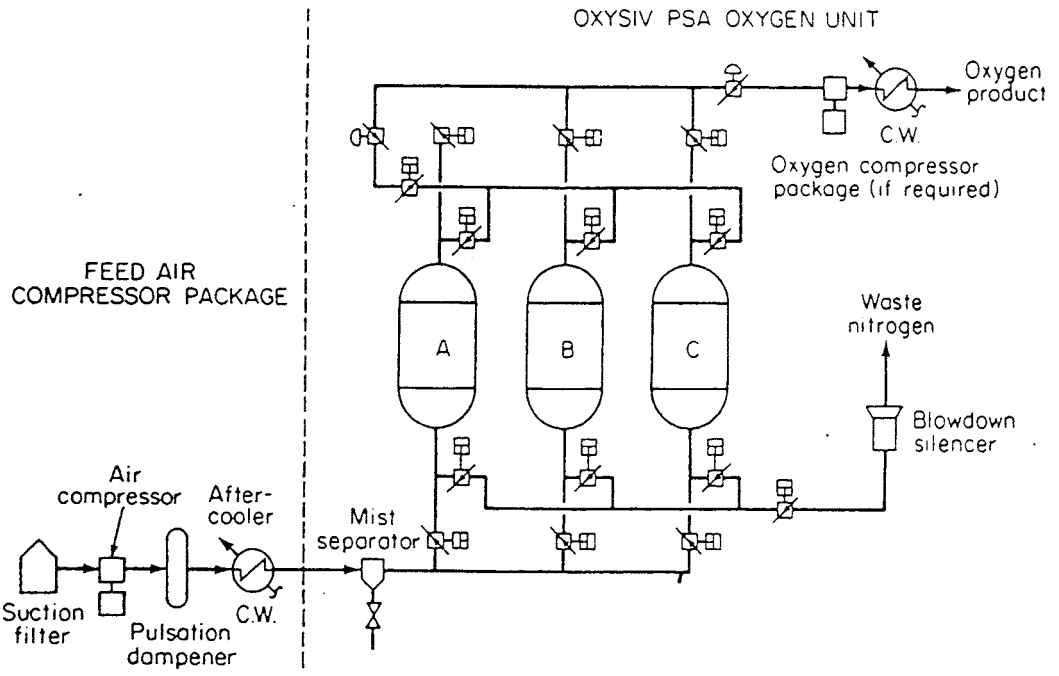

Fig. 4.7. Pressure-swing generation system, Union Carbide's "Oxysiv" PSA oxygen generation system.

aluminum, stainless steel, copper, and copper alloys. All low-temperature equipment is assembled, with piping, in one or more cold boxes heavily insulated with nonflammable materials.

Some oxygen is produced by a noncryogenic, pressure-swing adsorption process[30] using a molecular sieve as the adsorbent to separate oxygen from ambient temperature compressed air. This process produces oxygen ranging in purity from 90 to 95% in the capacity range of 1 to 60 t/day. This simple process eliminates the need for cryogenic equipment, feed dryers, regeneration heaters, and attendant utility and maintenance costs.

Union Carbide's patented PSA process (U.S. Patent 3,738,087) uses three vessels. In operation, each vessel cycles between two stages—adsorption and regeneration. One vessel adsorbs while the others regenerate, as shown in Fig. 4.7. When the adsorbing vessel achieves its capacity for impurities, the compressed air feed is automatically switched to another vessel. The first vessel then begins its regeneration cycle, which is accomplished in three successive steps: depressurizing, purging with product oxygen, and partial repressurization, after which the vessel is again ready for the adsorption stage.

Impurities are rejected during the depressurization and purge steps and vented into the atmosphere. Regeneration is completed at atmospheric pressure. Adsorption and regeneration are automatic and rely only upon pressure swings for operation. There is no need for costly heating or refrigeration. Automatic timers, pressure switches, and relays control cycling as well as product flow.

RARE GASES OF THE ATMOSPHERE

Oxygen and nitrogen are the primary components of the atmosphere, but air also contains nearly 1% argon and lesser amounts of neon, krypton, and xenon (Table 4.5). Argon, neon,

[30]Davis, Oxygen Separated from Air Using Molecular Sieve, *Chem. Eng.* 79 (23) 88 (1972); Shaner, *Production of Industrial Gases from the Air*, Union Carbide Corp. publication L-

krypton, and xenon are all produced commercially as by-products from large cryogenic air separation plants. The distillation of liquid air is normally performed in the double-column arrangement illustrated in Fig. 7.6. The rare gases are produced in side columns operated in conjunction with the standard double-column plant.

A combination of a double column and side rectification columns is used to produce argon. Since argon boils at a temperature just below oxygen, its concentration level builds up in the upper column at a point above the oxygen product level. The argon-rich vapor is withdrawn from the upper column at a point about one-third of the distance between the oxygen product and the nitrogen waste and is fed to a side argon column. The feed vapor is primarily an argon-oxygen mixture (with some nitrogen) and because of the close boiling points of the components, the argon column is operated at a relatively high reflux ratio. The liquid reflux from the argon column is returned to the upper column at the same point as the vapor withdrawal. The crude argon product is withdrawn from the top of the argon column. The side argon column is driven by expanded kettle liquid obtained from the bottom of the lower column. The vaporized kettle vapor is fed to the upper column at the same point as the low-pressure turbine air feed. The argon column condenser usually includes a small liquid drain to the upper column. The purpose of this liquid drain is to avoid hydrocarbon buildup in the argon condenser liquid reservoir, since this condenser is not protected by hydrocarbon adsorption traps, as is the case with the main plant condenser. All process streams handled by the argon column are returned to the main plant columns, with the exception of the crude argon product. The crude argon is further processed in a section of the plant usually referred to as the argon refinery The crude argon product contains oxygen and nitrogen impurities. The oxygen impurity is removed by the addition of hydrogen and subsequent catalytic combustion and gas drying to recover the water. The nitrogen impurity is removed by another distillation step that produces the refined argon product at a purity of 99.999%.

The primary application of argon is in metallurgical processes. One major use is as a shielding gas (from oxygen) in the welding of metals such as aluminum and stainless steel and in the refining of exotic metals such as zirconium, titanium, and many alloys. Another significant use of argon is as a filler gas for incandescent light bulbs. The chief process for the production of stainless steel is the "argon-oxygen decarburizing" process, which requires large quantities of argon.

Since neon boils at a considerably lower temperature than nitrogen, it normally collects in the dome of the main condenser as a noncondensable gas. It can be recovered by the addition of a side column. Neon has well-known applications as a filler gas for display lights. Much larger quantities are used in high-energy research. It is also finding increasing uses in instrumentation and as a safe low-temperature cryogen for specialty applications. A new use is evolving in deep-sea diving, where mixtures of neon and helium have shown many advantages.

Since krypton and xenon have high boiling points relative to oxygen, they normally accumulate in the liquid oxygen sump of the upper column of the main plant. The primary application of krypton is as a light bulb filler gas. Its thermal properties are more favorable than those of argon and lead to more effective light bulbs. Additionally, both krypton and xenon are used in instrumentation and research applications.

The very rare gases, neon, krypton, and xenon, are normally marketed by the industry as "specialty gases." Other specialty gas products include gases of unusually high purity for research purposes, instrumentation calibration standards, and special mixes serving the need of a specific industry or laboratory. Specialty gas departments of the industrial gas companies have several unique capabilities. Creating gas mixtures tailored to user requirements for purity and for accuracy of mixture formulation is one such capability. Packaging gases in any desired quantity is another capability. Shipments can be made throughout the range from a

single gaseous liter packaged in a glass bulb to highway tube trailers transporting 2800 m^3 and up. Also available is specialized equipment including valves, pressure and flow gages, regulators, etc., capable of metering and measuring gases with exceptional accuracies with minimal loss and without contamination.

HELIUM

The helium industry began with the discovery of helium at Dexter, Kan. about 1900, but it is now also available from certain fields located in Oklahoma and Texas. The first pilot plants were constructed to supply helium for the lighter-than-air airships of the Allies in World War I to replace highly flammable hydrogen. Helium has 92.5 percent of the lifting power of hydrogen. Another less widely known use has been in a mixture with oxygen to provide a synthetic atmosphere for deep-sea divers and tunnel workers. Substitution of helium for nitrogen prevents nitrogen narcosis, which occurs at water depths greater than 30 m.

In aerospace applications, helium is employed to purge and pressurize spacecraft. This was the largest market for helium in the mid-1960s.[31] Since then, there has been a rise in the relative importance of other markets, such as protective atmospheres in the fabrication of titanium, zirconium, and other metals, the growing of transistor crystals, and as a shielding gas for welding. Other uses include lead detection, cryogenic applications, and for generating ultra-low-temperature environments for superconducting devices. The annual consumption increased from 7.8×10^6 m^3 in 1962 to 26.9×10^6 m^3 in 1966 and then declined steadily to 12.7×10^6 m^3 in 1971. Consumption in 1980 in the United States was estimated at 18.2×10^6 m^3. The United States supplies 80 percent of the world's consumption and exports account for about one-quarter of domestic production. The Interior Department, in a government conservation program, is storing crude helium in underground reservoirs and, by 1981, 1.13×10^9 m^3 was stockpiled. This conservation effort is necessary because the helium is lost to the atmosphere when natural gas is consumed. Extraction of helium from the atmosphere would be extremely expensive. It is generally agreed that this valuable resource should be recovered and stored until the time that new energy technologies require vast amounts of helium. For various reasons, both governmental policy and economic, the Interior Department stopped purchasing helium from private producers in 1973. Since that time a lot of helium has been vented to the atmosphere. In an effort to stop this waste, a bill was introduced into Congress in 1980 to mandate that the Interior Department acquire helium for storage either by separating it from the government's Tip Top field or by purchasing it from private companies, or both. The bill set a storage goal of 1.8×10^9 m^3 by the end of 1985 and 2.4×10^9 m^3 by 1990.[32]

In 1981 6×10^6 m^3 of helium was produced and distributed to support federal programs such as NASA's space shuttle launches, the Department of Defense's advanced weapons research, and the Department of Energy's next-generation energy-conversion research. Of the gas thus distributed 2.8×10^6 m^3 was extracted from natural gas and 3.2×10^6 m^3 was

[31]Chopey, What's Next For Helium? *Chem. Eng.* 81 (12) 40 (1974).

[32]Anderson, Congress Renews Helium Conservation Effort, *Chem. Eng. News*, 58 (23) 11 (1980); Helium Conservation Drains Federal Funds, *Chem. Eng. News*, 47 (51) 46 (1969); ECT, 3d ed., vol. 12, 1980, pp. 249–287.

withdrawn from the Cliffside Gas Field which supplies the government reservoirs. Mobil Oil completed two wells in 1979 and 1980 in the Tip Top field in Sublette, Wyo. These wells are not currently in production, but the reserves in this field are estimated at 1.42×10^9 m^3. Almost all of the Tip Top field is on federal lands.

A typical plant removes the 2% helium from the natural gas in the pipeline that crosses the site, with an extraction efficiency of 92 to 95 percent. The pipeline gas enters at 3 to 4.5 MPa, is first scrubbed to take out water and condensable hydrocarbons, and is then passed through a gas cleaner, which removes pipeline dust. From the cleaner, the gas goes to absorption towers, where CO_2 is removed by a solution of MEA and diethylene glycol, and finally passes through a bauxite dryer. For the crude-helium-separation step, the purified gas enters large boxlike units, 12 m high with a cross section of 3 by 3 m, that operate in parallel. After entering one of the units, the gas is first chilled to −156°C by heat exchange with the exiting crude helium and depleted natural gas. The chilled stream is expanded into a separator-rectifier column, where, with the aid of a side stream of cold low-pressure nitrogen in a coil, the natural gas is liquefied and separated. The rectified, or crude-helium gas (75% helium, 25% nitrogen), passes through a heat exchanger counter to the incoming gas.

The depleted natural gas as a liquid passes from the bottom of the separator-rectifier through an expansion valve and also helps chill incoming feed gas, after which it leaves the unit, is compressed, and then returns to the gas pipeline. To provide cooling and to be usable in a cold side stream, high-pressure nitrogen is chilled by expansion and split into two parts. One of these is further cooled to about −179°C by expansion through two centrifugal turbo expanders located outside the separation unit box, and this cold stream then further chills the unexpanded portion of the original nitrogen stream.

To purify the crude-helium gas, the trace of hydrogen is first removed in a reactor with a small amount of air, where it is oxidized to water over a platinum catalyst. The hydrogen-free gas is further purified utilizing a pressure-swing adsorption (PSA) process. The PSA unit removes essentially all contaminants to very low levels, usually less than 10 ppm. Neon, however, is not removed by the PSA process, but for most helium uses it is not considered a contaminant.

Plants[33] are in operation to supply liquid helium (bp −268.9°C at 101 kPa compared with −252°C for hydrogen). The first plant at Amarillo, Texas produced 100 L/h. The Linde Division of Union Carbide Corp. assembled its plant inside a Dewar (i.e., thermos bottle) type of vessel 6 m high and 2.7 m in diameter. The difficulty is that *compressed helium does not exert the Joule-Thomson cooling effect upon expansion until −267°C is reached.* Helium gas is compressed to 1.9 MPa at 27°C where it enters the Dewar cold box. Here it is cooled to −187°C in the first of three fin-type aluminum heat exchangers against recycle helium and cold (−193°C) gaseous and liquid nitrogen. Next trace impurities are removed in a gel trap, and the gas stream is further cooled to −248°C in a heat exchanger against recycle helium. The effluent is split into two streams, so that the large stream can cool by expanding from 1.8 MPa to 27 kPa in an expander engine, thereby cooling itself to −260°C and thus providing a heat-exchange medium for further chilling the smaller fraction. Finally, the combined stream is chilled to −267°C by the recycle stream. Here the Joule-Thomson effect is positive and, by expanding from 1.8 MPa to 31 kPa, the helium cools itself in a separating vessel to liquefy about 15 percent of the helium at −268°C. The helium gas is recycled.

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[33]Chopey, Liquid-Helium Plant Tackles Gas That's Hardest of All to Liquefy, *Chem. Eng.* 69 (20) 76 (1962); Liquid Helium Plant, *Chem. Eng.* 70 (15) 86 (1963); Haul Helium Faster, *Chem. Week* 99 (8) 57 (1966).

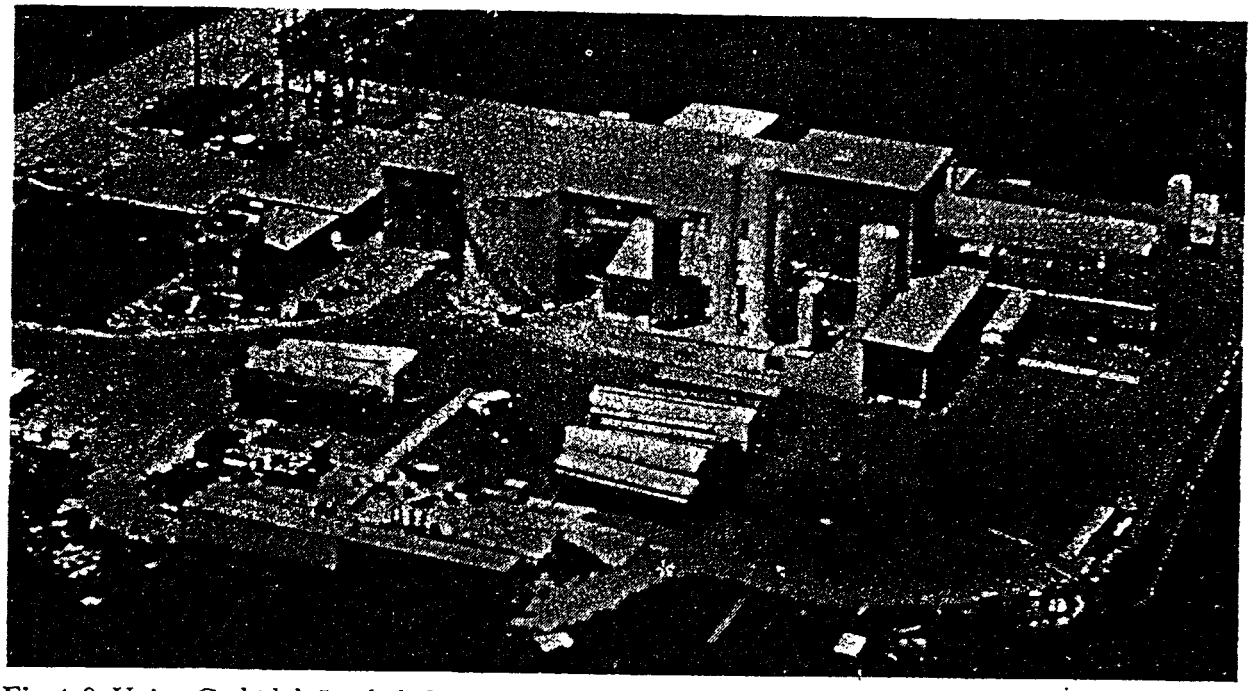

Fig. 4.8. Union Carbide's Linde helium production plant, Bushton, Kan.

The liquid-helium plant of the Kansas Refined Helium Co. at Otis, Kan. has an annual capacity of 6.1×10^6 L of liquid helium. This plant supplies the Air Reduction Co. (Airco) with liquid helium for distribution nationally. Airco has 38,000-L trailer trucks as well as special cryogenic containers for delivering this helium. Linde Division of Union Carbide Corp. has a plant at Bushton, Kan. as shown in Fig. 4.8.

ACETYLENE

USES AND ECONOMICS.[34] Acetylene is employed with oxygen to give a high welding temperature and in the manufacture of industrial chemicals such as vinyl chloride, acrylonitrile, polyvinylpyrrolidone, trichloroethylene, and acetic acid. Some of these compounds are also derived from other sources such as ethylene; only one chemical is made mostly from acetylene: chloroprene and its polymer neoprene. Studies of acetylene reactions at high pressures (the Reppe high-pressure technique) are very significant in that vinylation, ethynylation, and polymerization reactions have opened up a new field of chemistry by introducing many new compounds.

MANUFACTURE. Until recently all acetylene was made by the reaction of calcium carbide with water:

$$CaC_2(c) + 2H_2O(l) \rightarrow Ca(OH)_2(c) + C_2H_2(g) \qquad \Delta H = -126 \text{ kJ}$$

[34] Acetylene, *Chem. Eng. News* 40 (29) 54 (1963) (excellent use and production data); Miller, *Acetylene*, vol. 1, Academic, New York, 1965; Hardie, *Acetylene Manufacture Uses*, Oxford, New York, 1965; Sittig, *Acetylene Processes and Products*, Noyes, Park Ridge, N.J., 1968; Lorber et al., Acetylene Recovered from Ethylene Feedstock, *Chem. Eng.* 78 (15) 33 (1971); Baur, Acetylene from Crude Oil, *Chem. Eng.* 76 (3) 82 (1969) (process flowsheet); Acetylene from Coal Soon, *Chem. Eng.* 76 (6) 76 (1969).

There are two principal methods for generating acetylene from calcium carbide. The batch carbide-to-water, or wet, method takes place in a cylindrical water shell surmounted by a housing with hopper and feed facilities. The carbide is fed to the water at a measured rate until exhausted. The calcium hydroxide is discharged in the form of a lime slurry containing about 90% water. For large-scale industrial applications "dry generation," a continuous process featuring automatic feed, is popular. Here 1 kg of water is used per kilogram of carbide, and the heat of the reaction (6.2 MJ per cubic foot of acetylene) is largely dissipated by water vaporization, leaving the by-product lime in a dry, fairly easily handled state. Part of this can be recycled to the carbide furnaces. Continuous agitation is necessary to prevent overheating, since the temperature should be kept below 150°C and the pressure lower than 204 kPa.

The newest methods of manufacturing acetylene are through the *pyrolysis*, or *cracking, of natural gas* or liquid hydrocarbon feeds. The processes of most interest include partial oxidation, using oxygen, thermal cracking, and an electric arc to supply both the high temperature and the energy. An electric-arc procedure was used commercially at Huels, Germany. The free energy of acetylene decreases at higher temperatures. At 1600 K (1327°C) and higher, acetylene is more stable than other hydrocarbons[35] but decomposes into its elements. Hence conversion, or splitting, time must be incredibly short (milliseconds). The amount of energy needed is very large and in the region of the favorable free energy.

$$2CH_4(g) \rightarrow C_2H_2(g) + 3H_2(g) \qquad \Delta H_{1500°C} = +405 \text{ kJ}$$
$$CH_4(g) \rightarrow C + 2H_2(g) \qquad \Delta H = +85 \text{ kJ}$$

However, the decomposition of CH_4 into its elements starts at 850 K (578°C), hence competes with its degradation to acetylene. To lessen this degradation after raising the CH_4 (or other hydrocarbon) to a high temperature of about 1500°C for milliseconds, the reaction mass must be water-quenched almost instantaneously. Many flowcharts with technical data are depicted in ECT (loc. cit.) and also in the *1979 Gas Processing Handbook.*[36]

The partial combustion of natural gas is probably the method most used by experienced chemical manufacturers (Union Carbide, Tennessee Eastman, Monsanto, American Cyanamid, and Rohm & Haas). This is presented as a flowchart in Fig. 4.9 and embodies the chemical conversions just given. The process can be broken down into the following coordinated sequences:

Oxygen (90 to 98%) and natural gas are preheated separately to about 650°C, using fuel gas.

The two hot gases are conducted to and mixed in a burner or converter in a molar ratio of 0.60:100 for oxygen-methane.

The furnace or burner for this partial combustion consists of three parts: a mixing chamber, a flame or chemical-conversion zone, followed by a quench chamber with quench oil or water sprays. The chemical conversion is an almost instantaneous partial (two-thirds) combustion of the methane.

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[35]ECT, 3d ed. vol. 1, 1978, pp. 211–243 (tables and other thermodynamic and technical data); Leroux and Mathieu, Kinetics of the Pyrolysis of Methane to Acetylene, *Chem. Eng. Prog.* 57 (11) 54 (1961); Acetylene Flame Technology, *Chem. Eng. Prog.* 61 (8) 49–67 (1965) (four articles); Kampter et al., Acetylene from Naphtha Pyrolysis, *Chem. Eng.* 73 (5) 80 and 93 (1966) (flowchart and operating costs of high-temperature cracking).

[36]*Hydrocarbon Process.* 58 (4) 99–170 (1979).

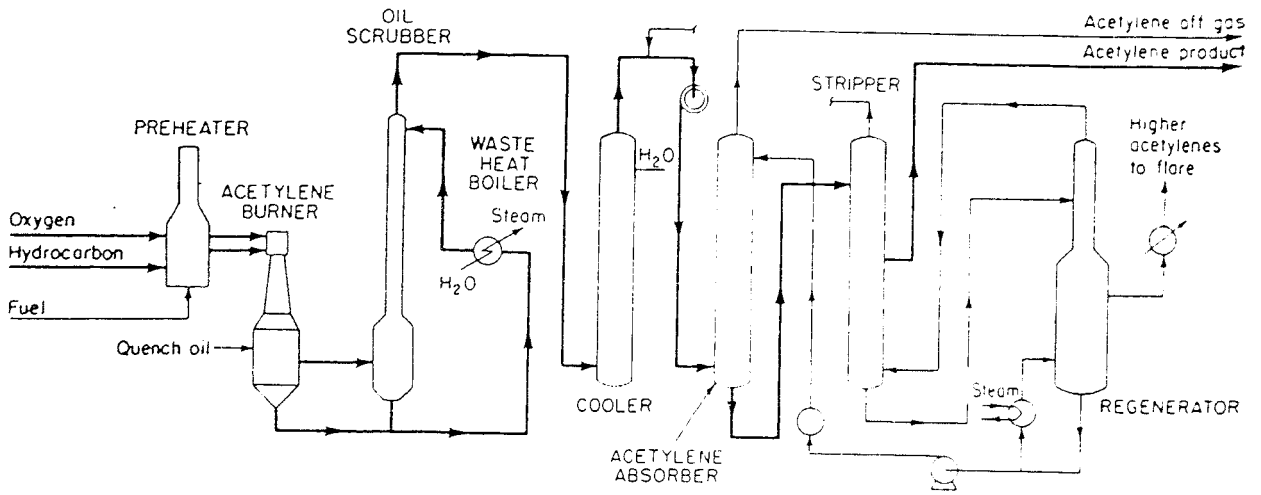


Fig. 4.9. Flowchart for acetylene by partial oxidation from hydrocarbon feedstock *(Chemical Construction Co.)*

Overall reaction of the methane (combustion and splitting) is 90 to 95%, whereas the oxygen is 100 percent converted. Residence time is 0.001 to 0.01 s. The acetylene and gases are cooled rapidly by quench oil or water sprays to 38°C and have the following typical composition, in percent:

Acetylene	8.5	Methane	4
Hydrogen	57	Higher acetylenes	0.5
Carbon monoxide	25.3	Inerts	1.0
Carbon dioxide	3.7	Total	100

The soot is removed in a carbon filter.

The clean gases are compressed to 1.14 MPa.

Acetylene is removed in a column (packed) by a selective solvent, e.g., dimethylformamide. Carbon dioxide is flashed and stripped overhead out of the rich solvent in a column (packed), where the acetylene is fractionated out, giving a 99%+ product with a 30 to 36 percent yield from the carbon in the natural gas.

Higher acetylenes and water are stripped out under reduced pressure, and the solvent is reused.

The Wulff process[37] for acetylene production used an arc furnace to pyrolyze hydrocarbons to acetylene. It has proved to be too expensive to compete now that energy costs have increased so much. It is described in CPI, 4th ed

Acetylene is also recovered from ethylene feedstock prior to ethylene polymerization.[38]

[37] *McGraw-Hill Encyclopedia of Science and Technology*, vol. 13, McGraw-Hill, New York, 1977, p. 270.

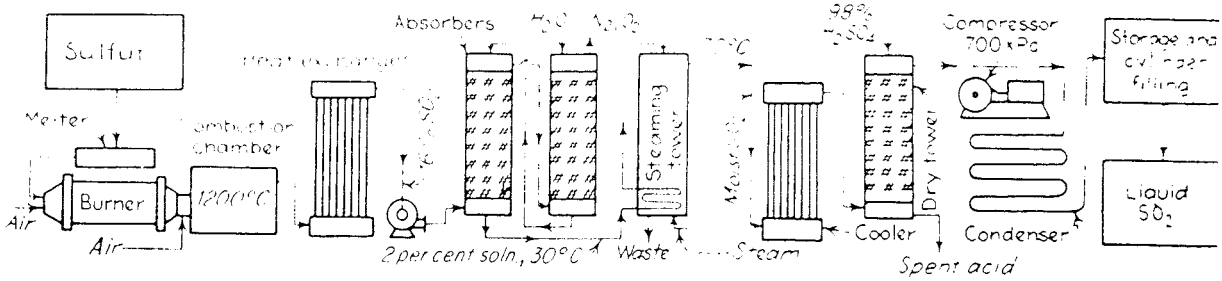
[38] Lorber, Reimann, and Rottmayr, Acetylene Recovered from Ethylene Feedstock, *Chem Eng.* **78** (17) 83 (1971).

SULFUR DIOXIDE[39]

Sulfur dioxide may be produced by the burning of sulfur or by the roasting of metal sulfides in special equipment. It may also be obtained by recovery from the waste gases of other reactions. Its production and the subsequent compression and cooling to form liquid sulfur dioxide, which boils at −10°C, are shown in Fig. 4.10. With very careful control of the amount of air entering the combustion chamber, sulfur dioxide can be produced up to 18% by volume at a temperature of 1200°C. As the gases from the combustion chamber pass through the heat exchanger, they heat the water for the boilers. The cooled gases, containing from 16 to 18% sulfur dioxide, are pumped into the absorbers through acidproof pumps. The strength of the solution from the absorbers is dependent upon the temperature and the strength of the gases entering, but the concentration usually runs about 1.3% with the temperature close to 30°C. A very small amount of sulfur dioxide is lost in the exhaust from the second absorber—about 0.02%. The temperature of the vapors coming from the steaming tower depends upon its design, but usually runs about 70°C. The vapors are cooled and passed through a drying tower in which 98% sulfuric acid is used. Other drying agents may be employed, and some plants by special procedure eliminate the use of this sulfuric acid dryer altogether. The sulfur dioxide is liquefied by compression to about 710 kPa and cooling. It is stored or put into cylinders.

Sulfur dioxide is shipped as a liquid under 200 to 300 kPa pressure. It is obtainable in steel cylinders of from 22- to 45-kg capacity, in 1-t tanks, or in 15-t tank cars. Its uses are numerous. A quite pure commercial grade, containing not more than 0.05% moisture, is suitable for most applications. A very pure grade, however, containing less than 50 ppm of moisture, is supplied for refrigeration. Sulfur dioxide also serves as raw material for the production of sulfuric acid. It finds application as a bleaching agent in the textile and food industries. Following the use of chlorine in waterworks and in textile mills, sulfur dioxide is an effective antichlor for removing excess chlorine. It is an effective disinfectant and is employed as such for wooden

[39]Yaws, Li and Kuo, Sulfur Oxides, *Chem. Eng.* 81 (14) 85 (1974); Potter and Craig, Commercial Experience with an SO_2 Recovery Process, *Chem. Eng. Prog.* 68 (8) 53 (1972); Profit in Stack Gas, *Chem. Week* 103 (3) 53 (1968).



In order to produce 100 kg liquid SO_2, the following materials and utilities are required.

Sulfur	54 kg	Electricity	1.5 MJ
H_2SO_4 (98%)	30 kg	Steam	340 kg
Water	7500 L	Direct labor	1.1 work-h

Fig. 4.10. Flowchart for liquid sulfur dioxide production.

kegs and barrels and brewery apparatus and for the prevention of mold in the drying of fruits. Sulfur dioxide efficiently controls fermentation in the making of wine. It is used in the sulfite process for paper pulp, as a liquid solvent in petroleum refining, and as a raw material in many plants, e.g., in place of purchased sulfites, bisulfites, or hydrosulfites.

CARBON MONOXIDE

Carbon monoxide is one of the chief constituents of synthesis gas. It is obtained in pure form through cryogenic procedures, with hydrogen as a coproduct. It is an important raw material in the production of methanol and other alcohols and of hydrocarbons. It is a powerful poison. It is used for making diisocyanate and ethyl acrylate by the following reactions:

$$2CO + 2Cl_2 \longrightarrow \underset{\text{Phosgene}}{2COCl_2} \xrightarrow{\text{toluene 2,4-diamine}} \underset{\text{Diisocyanate}}{CH_3C_6H_3(NCO)_2} + 4HCl$$

$$CO + CH{:}CH + C_2H_5OH \xrightarrow[HCl]{Ni(CO)_4} \underset{\text{Ethyl acrylate}}{CH_2{=}CHCOC_2H_5}$$

NITROUS OXIDE

Nitrous oxide is generally prepared by heating very pure ammonium nitrate to 200°C in aluminum retorts.

$$NH_4NO_3(c) \rightarrow N_2O(g) + 2H_2O(g) \qquad \Delta H = -36.8 \text{ kJ}$$

The purification consists of treatment with caustic to remove nitric acid and with dichromate to remove nitric oxide. It is shipped in steel cylinders as a liquid at a pressure of 10 MPa. It is used as an anesthetic, usually mixed with oxygen.

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Chapter 5

Industrial Carbon

The element carbon exists in three allotropic modifications, amorphous carbon, graphite, and diamond, which are employed industrially.[1] In general, carbon is chemically inert and is infusible at atmospheric pressure. Graphite and diamond resist oxidation even at high temperatures. Some industrial applications depend upon the chemical inertness of carbon. On the other hand, amorphous carbon can be activated, in which case it has a great capacity for selective adsorption from either the gaseous or liquid state. For nonmetallic substances, carbon and graphite possess very satisfactory electrical and heat conductivity. The heat conductivity of graphitized, coke-base carbon is superior to that of most metals. Both fabricated-amorphous and graphitic-carbon products have very low coefficients of thermal expansion and good thermal conductivity, giving them high resistance to thermal shock.

Carbon is an extremely versatile and useful element. Its applications grow each year. In 1928, Mantell[2] wrote, "The possibility of the expansion of carbon industries is very great, for they are intimately bound up with our highly complex life of the present day." This expansion has been realized.[3] The usefulness of carbon is apparent only when we single out the many phases of our everyday living where this adaptable element is essential: in the black pigment of the ink of our books, magazines, and newspapers; in carbon paper; in pencils; as the black color in many paints, automobile finishes, and shoe blacking; as a strengthening and toughening constituent of rubber tires, tubes, and other rubber goods, and as an *essential element in the construction of a very large amount of electrical and nuclear equipment*, from the household vacuum cleaner to the largest dynamos and nuclear reactors. The carbon arc is used in the production of visible and ultraviolet radiation in an increasingly large number of industrial processes dependent on photochemical reactions.

Nonfabricated industrial carbon is represented by lampblack, carbon black, activated carbon, graphite, and industrial diamonds. The first three are examples of *amorphous carbon*. *Lampblack* is soot formed by the incomplete burning of carbonaceous solids or liquids. It is gradually being replaced in most uses by *carbon black*, the most important of these amorphous forms and also the product of incomplete combustion. *Activated carbon* is amorphous carbon that has been treated with steam and heat until it has a very great affinity for adsorbing many materials. *Graphite* is a soft, crystalline modification of carbon that differs greatly

[1]Carbon as coal is considered in Chaps. 4 to 6.

[2]Mantell, *Industrial Carbon*, Van Nostrand, New York, 1st ed., 1928, and 2d ed., 1946.

[3]Riley, New World of Carbon and Graphite, *Mater. Des. Eng.* 56 (9) 113 (1962); Riley, *Graphite in Ceramics for Advanced Technologies*, Hove and Riley (eds.), Wiley, New York, 1965, pp. 14–75; Cahn and Harris, Newer Forms of Carbon and Their Uses, *Nature* 221 132–141 (1969); Walker and Throuer, *Chemistry and Physics of Carbon*, Marcel Dekker, New York, 1973.

in properties from amorphous carbon and from diamond. *Industrial diamonds*, both natural and synthetic, are used for drill points, special tools, glass cutters, wire-drawing dies, diamond saws, and many other applications, where this hardest of all substances is essential.

LAMPBLACK

Lampblack,[4] or soot, is an old product, made for many years by the restricted combustion of resins, petroleum, or coal-tar by-products. It has gradually been replaced in the pigment trade, particularly in the United States, by carbon black, which has superior tinting strength and coloring qualities, but in the manufacture of carbon brushes for electrical equipment and lighting carbons, lampblack is still a very important constituent. Its color is bluish gray black, rather than the deep black of carbon black; this steely black is desirable for some metal polishes and for pencils. Annual production is estimated to be less than 13,000 t.[4a]

In the United States either tar oils or petroleum oils are burned with a restricted amount of air to form soot, or lampblack. The soot is collected in large chambers from which the *raw* lampblack is removed, mixed with tar, molded into bricks, or *pugs*, and calcined up to about 1000°C to destroy bulkiness. The calcined pugs are ground to a fine powder. Some furnaces remove empyreumatic impurities by calcination in the gas stream of the furnaces where formed. Lampblack process development in recent years has evolved along lines similar to that of the oil furnace carbon black process (to be discussed later).

Carbon brushes for use in electric machinery are made by mixing lampblack with pitch to form a plastic mass. Petroleum coke or graphite may be added to this mix to impart special properties. Plates or blocks from which the brushes are later machined are formed by extrusion or high-pressure molding, and these *green* plates are then baked at a high temperature for several days to drive off volatile matter.

When carbons for the production of special arc lights are desired, a mixture of petroleum coke and thermally decomposed carbon is extruded in the form of a tube. This tube is baked at 1450°C, and a *core* of selected material is forced into its center and calcined again. The type of radiation emitted by the arc is largely dependent on the core material employed, which is frequently a mixture of lampblack flour, rare-earth oxides, and fluorides, with coal tar as a binder. Many millions of such lighting carbons are sold each month in peacetime for movie projectors. In war years, a great quantity of such lighting carbons was used in searchlights.

CARBON BLACK

The first factory for the making of carbon black[5] in this country was built at New Cumberland, W. Va., in 1872. The black was produced by cooling a burning gas flame against soapstone slabs and scraping off the carbon produced. In 1883, the roller process was patented

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[4]ECT, 2d ed., vol. 4, 1964, pp. 254–256; 3d ed., vol. 4, 1978, p. 653; Mantell, *Carbon and Graphite Handbook*, Interscience, New York, 1968, chap. 5.

[4a]t = 1000 kg.

[5]Until this date, lampblack was the only commercially available form of "carbon black," which is the most commonly accepted generic term for the entire family of colloidal carbons. Carbon black and lampblack are similar chemically, but they differ greatly in particle size and shape. ECT, 3d ed, 1978, vol. 4, p. 632.

and, in 1892, McNutt perfected the channel process. Early production was moderate, 12,000 t. In 1904 the reinforcing effect carbon black imparts to rubber was reported by S. C. Mote in England. In the summer of 1912, the B. F. Goodrich Co., convinced of the value of carbon black in the rubber industry, sampled a carload of the material and later that year placed an order for 500 t/year. The advent of this new market stimulated the industry. Expansion was rapid, and natural gas was the initial raw material. The first thermal black process was patented in 1916, and production began in 1922; the gas furnace made its commercial debut in 1928. In November 1943, the first oil furnace black plant went on stream in Texas. In 1974 the Charles Goodyear Award Medal of the Rubber Division of the American Chemical Society was presented to J. C. Krejci in recognition of his pioneering work on the oil furnace process.

The selling price of carbon black has been greatly reduced as the industry has expanded. In 1872 the price was $5.50 per kilogram and by 1967 it had dropped to 13 cents per kilogram. However, prices increased again because of greatly increased petroleum prices and general inflation. In 1981 prices of carbon black ranged between 70 and 84 cents per kilogram. The growth of the U.S. carbon black market is shown in Fig. 5.1. The current decline is a result of the essentially one-product use of carbon black, i.e., automobile tires. The auto industry is in a period of decreased sales thus limiting the demand for tires, and the advent of smaller cars has meant smaller tires and thus a smaller demand for carbon black. Radial tires are much longer wearing than the older types and therefore demand for replacement tires has greatly decreased. This decline in demand, as well as sharply increased prices for feedstock, has led to the shutdown of several old, inefficient plants in an effort to maintain a profitable basis for the remaining plants.[6]

Carbon black is a very finely divided, essentially nonporous type of carbonaceous material which is produced in a precisely controlled pyrolytic petrochemical process. The best rubber-grade blacks are spherical carbon particles (ranging from about 10 to 75 nm in diameter) fused together in grapelike clusters. Each particle is composed of several thousand microcrystallite bundles which are stacked together in a random (turbostratic) order.[7] Each bundle

[6]Schell, Black Days for Carbon Black, *Chem. Business*, Dec. 14, p. 49, 1981.

[7]Deviney, Surface Chemistry of Carbon Black and Its Implications in Rubber Chemistry, *Advan. Colloid Interface Sci.* 2 237–259 (1969).

Fig. 5.1. Growth of U.S. carbon black market, 1970–1981

consists of three to five micrographitic planes or platelets, elliptical-shaped and with axis lengths of about 1.5 to 1 nm, which are stacked in a not quite parallel manner. The 0.348- to 0.356-nm interlayer spacing is slightly greater than that of graphite (0.3354 nm).

About 50 to 80 percent of the carbon atoms in carbon black are thought to be present in the microcrystallite bundles, while the remainder is disorganized carbon. At the carbon surface, oxygen, sulfur, and sometimes other elements interact with the hydrogen positions of the polynuclear aromatic platelets, forming complexes that are generally analogous to classes of compounds of organic chemistry (e.g., carboxylic acid, phenolics, quinones, etc.). The oxygen content of most rubber-grade oil furnace blacks is usually below 1% but is higher (3 to 8%) for ink-grade types.

USES AND ECONOMICS. About 94 percent of the domestic carbon black consumption is in rubber products, especially tires (67 percent of total), heels, and mechanical goods, where it is used to improve wearing qualities by imparting toughness. Carbon black has made possible the adoption of synthetic rubber [especially styrene-butadiene (SBR) copolymer] for automobile tires. High-abrasion furnace blacks, when combined with "cold-polymerized" SBR, produce tire treads that consistently give better wear than controls compounded with natural rubber and channel blacks. The rubber compound in modern tires contains about 35% carbon black, which accounts for the rubber industry's role as the leading consumer of carbon black. Most printing inks are also based on carbon black. In this case the blacks must be uncompressed, grind easily, and absorb oil readily. The pigments in black plastics, paints, lacquers, and enamels are usually carbon black. Color-grade blacks used for inks and paints were once produced almost exclusively by the channel process but have been largely replaced by furnace blacks, particularly chemically and air-oxidized types. Even typewriter ribbons and carbon papers employ this pigment.

MANUFACTURE. The four basic carbon black manufacturing processes are either of the partial combustion type (the channel, oil furnace, or gas furnace process) or of the cracking type (the thermal process). By the early 1970s, the oil furnace process had become dominant, and most (about 90 percent) of the world's carbon black is now manufactured by this process, which uses aromatic petroleum oils and residues as feedstock (cf. Table 5.1). The ever-increasing cost of natural gas led to the shutting down of all channel black plants in the United States by 1976.

Table 5.1 Comparison of Carbon Black Processes

	Channel	Gas Furnace	Oil Furnace	Thermal
Raw material	Natural gas	Natural gas	Liquid aromatic hydrocarbons	Natural gas
Commercial yield, g/m^3	8–32	144–192	300–660	160–240
Yield, % theoretical C content	1.6–6.0	27–36	23–70	30–45
Energy utilization in manuf., J/kg	$1.2–2.3 \times 10^9$	$2.3–3.0 \times 10^8$	$9.3–16 \times 10^7$	$2.0–2.8 \times 10^8$
No. U.S. producers, 1979	0	n.a.*	7	2
Production 1980, t	0	n.a.	1.8×10^9	0.45×10^6

*n.a., Not available, but probably very small

For historical interest, the *channel black process* will be briefly described. These blacks ar produced when underventilated natural gas flames impinge upon 20- to 25-cm "chann irons," which are slowly reciprocated over scrapers to remove soot deposits. The type of blac produced was controlled by burner-tip design, burner-to-channel distance, and air suppl (degree of partial combustion). Yields were always poor, varying from 5 percent for som rubber grades to only 1 percent for high-color ink grades. Particle diameters ranged from 1 to 30 nm (compared with 18 to 75 nm for oil furnace blacks), and the oxygen content wa greater than, and the sulfur percentage less than, that of corresponding furnace blacks.

In addition to the low yield and natural gas cost factors, the rapid demise of the chann process was caused by high steel and capital investment requirements, severe pollution prol lems, and somewhat poorer performance in synthetic rubber (compared with furnace blacks

In the *thermal black process*, natural gas is cracked to carbon black and hydrogen at 110 to 1650°C in a refractory-lined furnace in a two-cycle (heating and "making" or decomp sition) operation. The reaction is

$$CH_4 \rightarrow C(amorph) + 2H_2(g) \qquad \Delta H = +85 \text{ kJ}$$

The large thermal blacks (140 to 500 nm) are essentially spherical, contain little chem sorbed surface oxygen, and are mainly used in special rubber applications. Yields are abou 30 to 45 percent, and thermal blacks accounted for slightly less than 4 percent of the tota U.S. carbon black production in 1980.

In the *oil furnace process*, a highly aromatic feedstock oil (usually a refinery catalyti cracker residue, although some coal tar–derived material is also used) is converted to th desired grade of carbon black by partial combustion and pyrolysis at 1400 to 1650°C in refractory (mainly alumina)-lined steel reactor. Two carbon black properties of vital impor tance in rubber applications—particle size and "structure" (the degree of particle fusion o reticulation into three-dimensional chain networks)—are closely controlled through nozzl design, reaction chamber geometry, temperature, residence time, and intensity of gaseou turbulence.

A schematic of the oil furnace process and a reactor is shown in Fig. 5.2. Basically, th heavy aromatic feedstock oil is atomized and sprayed through a specially designed nozzl into a highly turbulent combustion gas stream formed by preburning natural gas or oil witl about a 50 percent excess of air. Insufficient air remains for feedstock combustion, and th oil spray is pyrolyzed in a few microseconds into carbon black with yields (based on carbon varying from 65 to 70 percent for large carcass-grade types down to about 35 percent fo small tread-grade types, which impart maximum abrasion resistance to SBR and other syn thetic elastomers.

The black "smoke" from the reaction chamber enters the tunnel where, 1 to 3 m down stream, it is water-quenched to about 200°C. Tunnel and combustion chamber dimension vary, but frequently are from 2 to 6 m for length and from 0.1 to 1 m for internal diameter Further downstream, precipitators, cyclones, and to a greater extent bag filters (insulated t remain above 100°C) are used to separate the product black from water vapor and the com bustion off-gases. With modern fiberglass bag filters, carbon black recovery efficiency is essen tially 100 percent. Following pulverization and grit removal steps, the loose, fluffy black i normally pelletized for convenient bulk handling and to reduce the tendency to dust. In the commonly used wet pelletizing process, the black is agitated and mixed with water in a trough containing a rotating shaft with radially projecting pins, which form the pellets. The

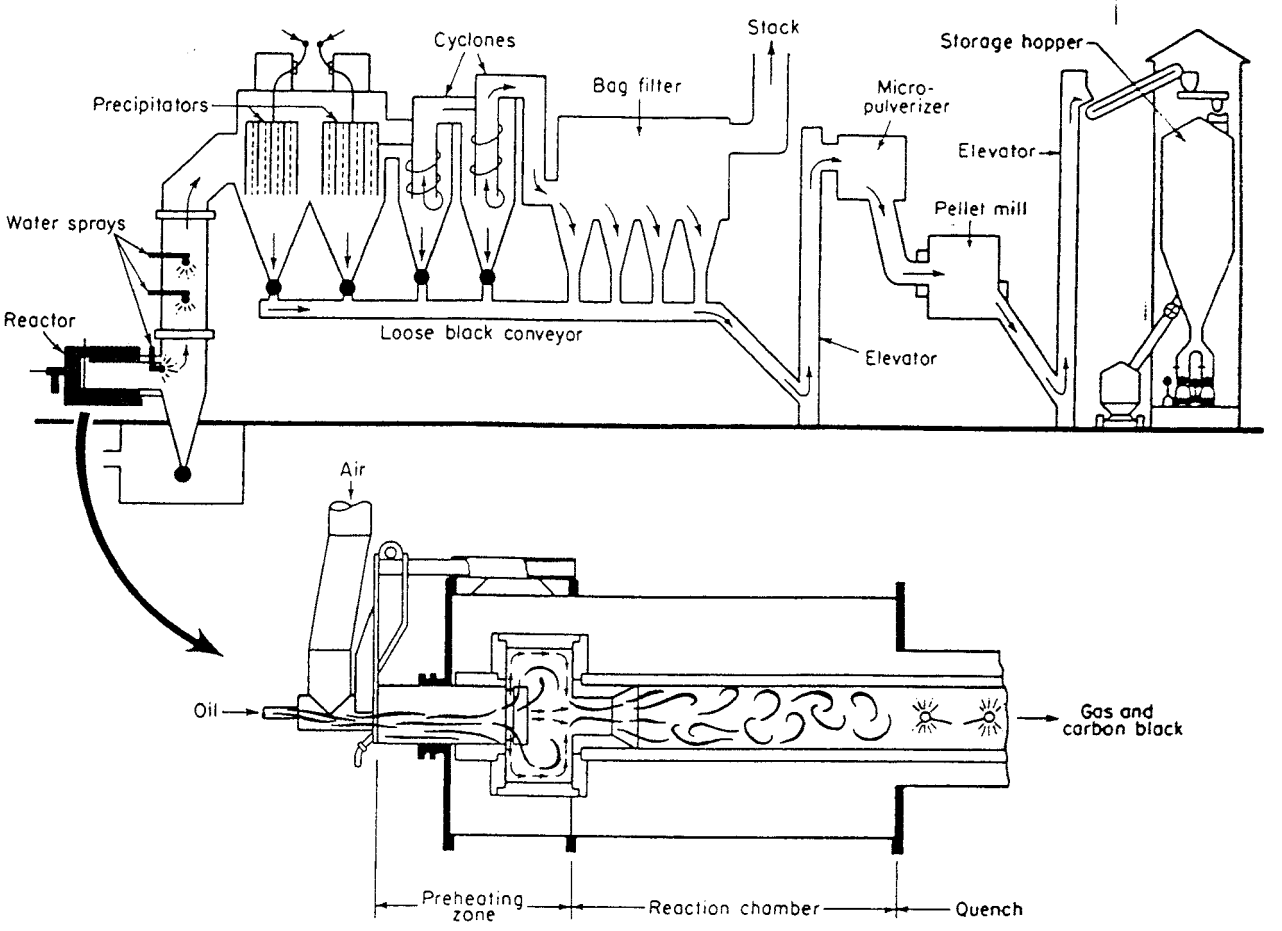

Fig. 5.2. Flowchart, carbon black furnace process. [*Chem. Week* 88 *(24) 79 (1962).*]

wet pellets, usually in the 25- to 60-mesh range, are dried in a gas-fired rotating-drum dryer. In the dry pelletizing process, pellets are formed by gentle agitation and rolling (10 rpm) of the black in horizontal rotating drums (about 3 m in diameter and 6 to 12 m long) for periods of 12 to 36 h. An oil pelletizing process is also used, to a minor extent, for specialty applications (e.g., certain ink-grade blacks).

Furnace blacks are divided into tread grade (18- to about 38-nm diameter) and carcass grade (44- to about 75-nm diameter) types. Specific grades are now designated according to a three-digit numbering system (ASTM D 2516) in which the first digit refers to the particle diameter range, as measured with an electron microscope. For example, the old SAF (super abrasive furnace) black is now N-110, the first digit designating a 11- to 19-nm particle diameter, while the former FEF-LS (fast extrusion furnace-low structure) is now N-539, the 5 designating a particle diameter of 40 to 48 nm. The *gas furnace process*, similar to the oil furnace process but based on natural gas as feedstock, has been almost completely replaced by the latter, which is capable of reproducing all gas furnace–grade blacks.

Acetylene black, a special type of thermal black used in dry cell batteries and for imparting electrical and thermal conductivity to plastics and rubber, is produced by acetylene decomposition (in the absence of air) at about 800°C in a continuous exothermic process. This material (of about 42-nm particle diameter) is the purest form of carbon black and has low surface activity, low moisture adsorption, high liquid adsorption, and high electrical and thermal conductivities.

ACTIVATED CARBON[8]

Activated carbon first came into prominence through its use as an adsorbent in gas masks in World War 1. However, the knowledge that carbon produced by the decomposition of wood can remove coloring matter from solutions dates back to the fifteenth century. The first commercial application of this property, however, was not made until 1794, when charcoal filters were used in a British sugar refinery. About 1812, bone char was discovered by Figuer. Activated carbons can be divided into two main classes: those used for adsorption of gases and vapors, for which a granular material is generally employed, and those used in purification of liquid, for which a powdered material is desired.

USES. There is no particular activated carbon that is effective for all purposes. As a decolorant, activated carbon, with its very great surface area and pore volume, is hundreds of times more efficient than charcoal and at least 40 times more than bone black. The specific surface area ranges from 300 to 2500 m^2/g. The amount of material adsorbed by activated carbon is surprisingly large, amounting frequently to from a quarter to an equal weight of such vapors as gasoline, benzene, and carbon tetrachloride. These substances can be recovered and reused. Adsorption[9] is a physical phenomenon, depending largely upon surface area and pore volume. The pore structure limits the size of molecules that can be adsorbed, and the surface areas developed limit the amount of material that can be adsorbed, assuming suitable molecular size.

The major use[10] of activated carbon is in solution purification, such as the cleanup of cane, beet, and corn sugar solutions, and for the removal of tastes and odors from water supplies, vegetable and animal fats and oils, alcoholic beverages, chemicals, and pharmaceuticals. The recovery of streptomycin represents a typical application of the continuous treatment of liquids.

The vapor-adsorbent type of activated carbon was first used in gas masks because of its ability to adsorb certain poisonous gases, and it is now widely employed in both military and industrial gas masks. Activated carbon is used in air conditioning systems to control odors in large restaurants, auditoriums, and airport concourses. An important field of application is the industrial recovery and control of vapors (Fig. 5.3). The recovery of such vapors amounts to millions of kilograms per year, with a recovered value of several hundred million dollars. Activated carbon is able to adsorb practically any organic solvent at about 35°C and release it when heated to 120°C or higher for solvent recovery. One of the largest uses is for gasoline vapor emission control cannisters in automobiles. Specially impregnated grades are used in cigarette filters. Activated carbon can now be made in an extruded form, which in vapor

[8]ECT, 3d ed., vol. 4, 1978, pp. 561–70.

[9]For an excellent discussion of adsorption, see Perry, sec. 16, Adsorption and Ion Exchange.

[10]Browning, New Water-Cleanup Roles for Powdered Activated Carbon, *Chem. Eng.* 79 (4) 36 (1972); Erskine and Schuliger, Activated Carbon Process for Liquids, *Chem. Eng. Prog.* 67 (11) 41 (1971): Barnebey, Activated Charcoal in the Petrochemical Industry, *Chem. Eng. Prog.* 67 (11) 45 (1971); Storck, Activated Carbon Growth Tied to Water Rules, *Chem. Eng. News* 56 (16) 10 (1977); Sansone, Jonas, and O'Brien, Prediction of Removal Efficiency of Activated Carbon, *Carbon* 19 (3) 231 (1981).

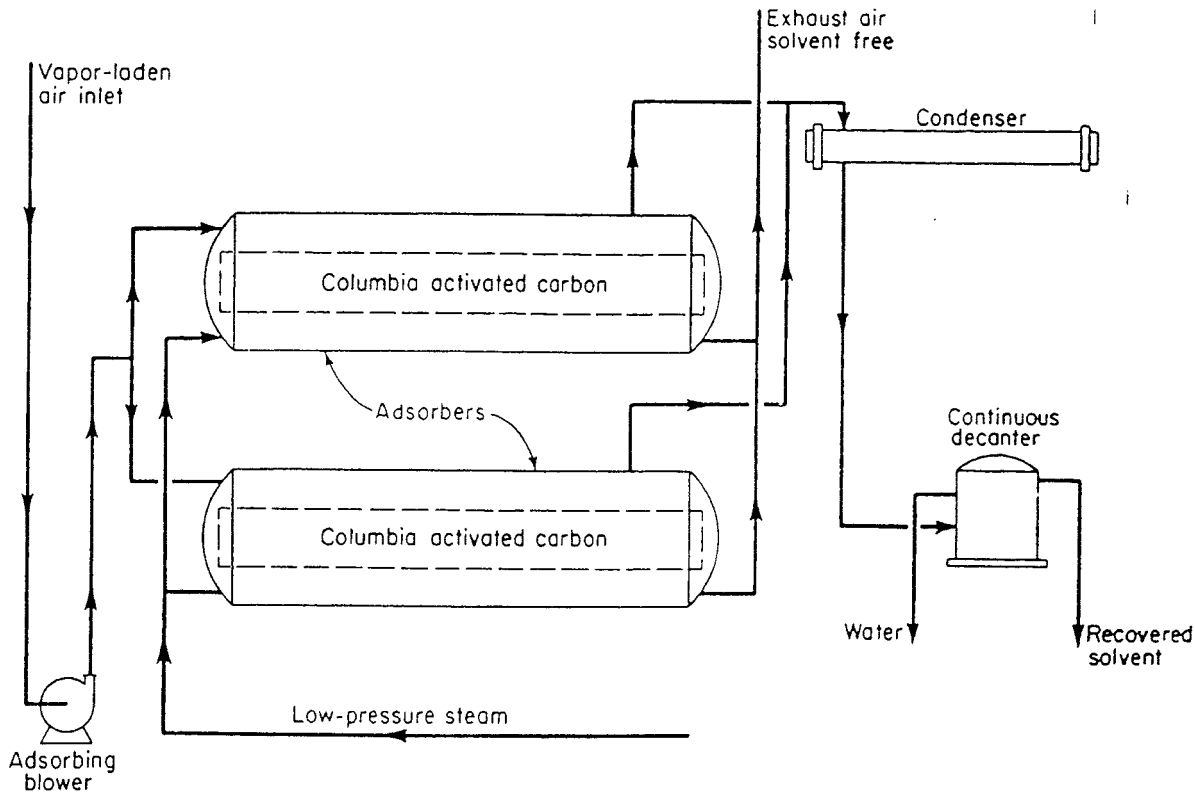

Fig. 5.3. Flowchart of one type of solvent recovery plant employing Columbia activated carbon. A typical plant of this type in recovering a hydrocarbon vapor at a rate of 500 kg/h from 370 m^3/min of vapor-laden air has the following approximate average utility requirements per kilogram of recovered solvent: steam, 3.5 kg; water, 55 L; electric power, 396 kJ. *(Union Carbide Corp., Carbon Products Div.)*

adsorbing presents only about half the air resistance of the older granulated heterogeneous powder. The pressure drop through carbon, whether pelleted or granular, depends primarily on the average particle size. Pelleted material ensures more uniform packing, hence more even distribution of air flow.

MANUFACTURE. Many carbonaceous materials, such as petroleum coke, sawdust, lignite, coal, peat, wood, charcoal, nutshells, and fruit pits, may be used for the manufacture of activated carbon, but the properties of the finished material are governed not only by the raw material but by the method of activation used. Decolorizing activated carbons are usually employed as powders. Thus the raw materials for this type are either structureless or have a weak structure. Sawdust and lignite yield carbons of this kind. Vapor-adsorbent carbons are used in the form of hard granules and are generally produced from coconut shells, fruit pits, or briquetted coal and charcoal. The most important physical property is the surface area.

Activation is a physical change wherein the surface of the carbon is tremendously increased by the removal of hydrocarbons. Several methods are available for this activation. The most widely employed are treatment of the carbonaceous material with oxidizing gases such as air, steam, or carbon dioxide, and the carbonization of the raw material in the presence of chemical agents such as zinc chloride or phosphoric acid. Essentially all activated carbons produced in the United States are made by the steam activation method. The chemical activation method is still practiced extensively in European and other countries. Amoco has developed

a powdered activated carbon (superactive carbon) which has 200 to 400 times greater surface area than the usual grades.[11]

Gaseous-oxidation activation employs a material that has been carbonized at a temperature high enough to remove most of the volatile constituents but not high enough to decompose the evolved gases. The carbonized material is subjected to the action of the oxidizing gas, usually steam or carbon dioxide, in a furnace or retort at 800 to 980°C. Conditions are controlled to permit removal of substantially all the adsorbed hydrocarbons and some of the carbon, so as to increase the surface area. The use of chemical impregnating agents causes the carbonization to proceed under conditions that prevent the deposition of hydrocarbons on the carbon surface. The raw material generally used is sawdust or peat, which is mixed with the chemical agent, dried, and carbonized at temperatures up to 850°C. When the carbonization has been completed, the residual impregnating agent is removed by leaching with water.

Regeneration. After activated carbon has become saturated with a vapor or an adsorbed color, either the vapor can be steamed out, condensed, and recovered as shown in Fig. 8.3, or the coloration can be destroyed and the carbon made ready for reuse. The oldest example of this process uses the decolorizing carbon long known as *bone char*, or *bone black*. This consists of about 10% carbon deposited on a skeleton of tricalcium phosphate and is made by the carbonization of fat-free bones in closed retorts at 750 to 950°C. A new process for regenerating activated carbon, *atomized suspension*, involves making a slurry of the spent powdered carbon with water and atomizing the slurry in an oxygen-free chamber and heating above 650°C to pyrolyze the adsorbed contaminants.[12]

NATURAL GRAPHITE[13]

Graphite, as it occurs naturally, has been known to humans for many centuries. Probably its first use was for decorative purposes in prehistoric times. By the Middle Ages it was being employed for writing and drawing purposes. The name graphite was given to this substance by the mineralogist Werner in 1879. Natural graphite occurs throughout the world in deposits of widely varying purity and crystalline size and perfection. For import purposes, natural graphites are classified as *crystalline* and *amorphous*. The latter is not truly amorphous but has an imperfect lamellar microcrystalline structure.

Foundry facings constitute the largest single use of natural graphite; this application, steelmaking, refractories, and crucibles account for approximately 70 percent of U.S. consumption. Lubricants, pencils, brake linings, and batteries account for approximately 20 percent. The U.S. production of natural graphite has been small in recent years but a considerable amount is imported.

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[11]*Chem. Week* 120 (7) 40 (1977).

[12]Spent Carbon Gets New Lease on Life, *Chem. Week* 18 (2) 44 (1976).

[13]ECT, 3d ed., vol. 4, 1978, pp. 556–708.

MANUFACTURED GRAPHITE AND CARBON

Natural graphite was the only kind available, except in laboratory quantities, until 1896, when Edward G. Acheson invented the first successful process for the commercial production of artificial graphite, as an outgrowth of his work on silicon carbide. He discovered that when most forms of amorphous carbon are placed in an electric furnace with certain catalysts such as silica or alumina and subjected to a temperature of approximately 3000°C, they are converted into the allotrope graphite. It is now known that the industrial process converts amorphous carbon directly to graphite in an electric furnace. In the carbon industry, the term "carbon" is normally used for carbonaceous materials that have been heated to 1000 to 1300°C; the term "graphite" is used for materials heated to greater than 2500°C. Only the coke from petroleum or pitch can be used to manufacture graphite; lampblack does not graphitize.

USES AND ECONOMICS.[14] Since they combine chemical resistance with a variety of physical properties desirable in chemical-plant structural materials, carbon and graphite are among the most widely used nonmetallics in this field. They are both highly resistant to thermal shock, and graphite has unusually high thermal conductivity (Fig. 5.4). This, combined with excellent machinability, makes graphite and impervious graphite the preferred choice for many items of chemical equipment. Impervious graphite (or impervious carbon) is made by impregnating the somewhat porous base graphite (or carbon, if impervious carbon is to be produced) with a synthetic resin. The impregnation employs a vacuum-pressure cycle for complete resin penetration. The resin generally used is a phenolic type, which is polymerized by curing at elevated temperatures in steam-heated autoclaves.

[14]Schley, Impervious Graphite for Process Equipment, *Chem. Eng.* **81** (4) 144; **81** (6) 102 (1974).

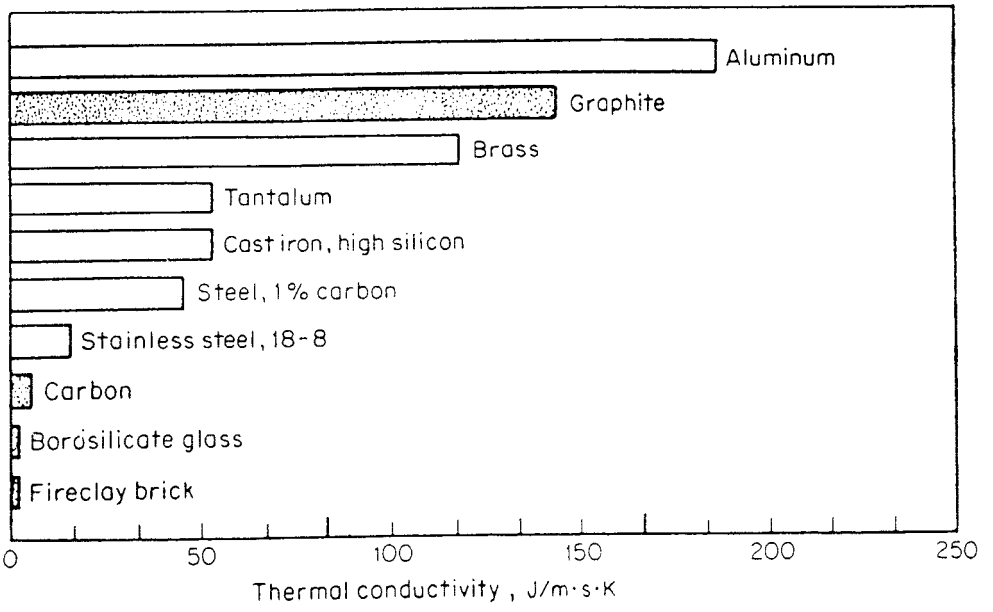

Fig. 5.4. Thermal conductivity of common materials of construction.

The chemical resistance of impervious graphite and impervious carbon materials produced in this manner is practically identical with that of the original stocks. The graphitic materials are recommended for use at material body temperatures up to 170°C. Graphite is recommended for use with practically all mineral acids, salt solutions, alkalies, and organic compounds at temperatures up to boiling. The only exceptions are when strong oxidizing conditions exist, such as with sulfuric acid above 96% concentration, nitric acid, strong chromic acid, bromine, fluorine, and iodine. Cements for assembling graphite use resins similar to those which produce the impervious material. Permanent weldlike joints are formed with corrosion resistance and strength equivalent to or stronger than that of the basic material.

Carbon and graphite are most commonly used in the form of brick and large blocks or plates for chemical-process applications. Single-piece shapes are made routinely in diameters up to 170 cm and in lengths up to 200 cm. Figure 5.5 shows typical large-block construction with carbon and graphite. The Quonset-hut type of structure is a graphite chamber for the combustion of phosphorus with oxygen to form P_2O_5, which is then hydrated in the silolike carbon structure alongside to form phosphoric acid. Similar construction is used for linings of sulfuric acid concentrators and for electrostatic precipitators, where dimensional stability is important. Tank linings of carbon brick are encountered in metal pickling, cleaning, and finishing work, particularly where exposure to hydrofluoric acid is involved, and in the digestion of phosphate rock with sulfuric acid in the manufacture of phosphate fertilizers.

Mold-grade graphite is the most important of the carbon and graphite structural materials to the chemical industry. Graphite's easy-machining qualities, together with its availability in many sizes and shapes, permits construction of a complete range of process equipment, including heat exchangers, pumps, valves, pipes and fittings, towers, and absorbers. Graphite's high thermal conductivity (Fig. 5.4) is particularly important in heat-exchange applications. Most common of the standard constructions are the conventional shell-and-tube heat exchangers, shown in Fig. 5.6, which range in size to units having as much as 1400 m^2 of transfer surface. Operating pressures range up to 700 kPag, with steam pressures of 350 kPag. Other uses of impervious graphite include plate and block-type heat exchangers, cascade coolers, and centrifugal pumps.

Graphite is being used for rocket nozzles, and wing leading edges and nose cones of reentry vessels because of its light weight and good mechanical strength at extremely high temperatures.

Recently, new flexible and compressible types of graphite have been developed that contain no binders, resins, or other additives and that have the chemical inertness and lubricity typical of pure graphite. These materials can be made in sheets and tapes, as well as in laminates and foam. Uses in chemical-process equipment include high-temperature and corrosion-resistant packing and gaskets, and high-temperature thermal insulation, where the unique anisotropic properties can be used to advantage.

Electrothermic applications, such as the production of steel in the electric open-arc furnace, as well as the production of ferroalloys and phosphorus in submerged-arc furnaces, account for the largest consumption of preformed carbon and graphite electrodes. Graphite electrodes for open-arc furnaces may be as large as 60 cm wide and 245 cm long while the carbon and semigraphite (carbon plus graphite filler) electrodes for submerged-arc furnaces are typically 140 cm wide and 265 cm long. *Electrolytic* applications include anodes for fused-salt electrolysis to produce aluminum, magnesium, and sodium metals, as well as electrolysis of aqueous brines to produce chlorine, caustic soda, and chlorates. Flowcharts for these applications are given in other chapters. Carbon and graphite's increased strength at elevated temperatures, their immunity to thermal shock, their resistance to the corrosive effects of molten slags, and the failure of most molten metals to wet them account for their

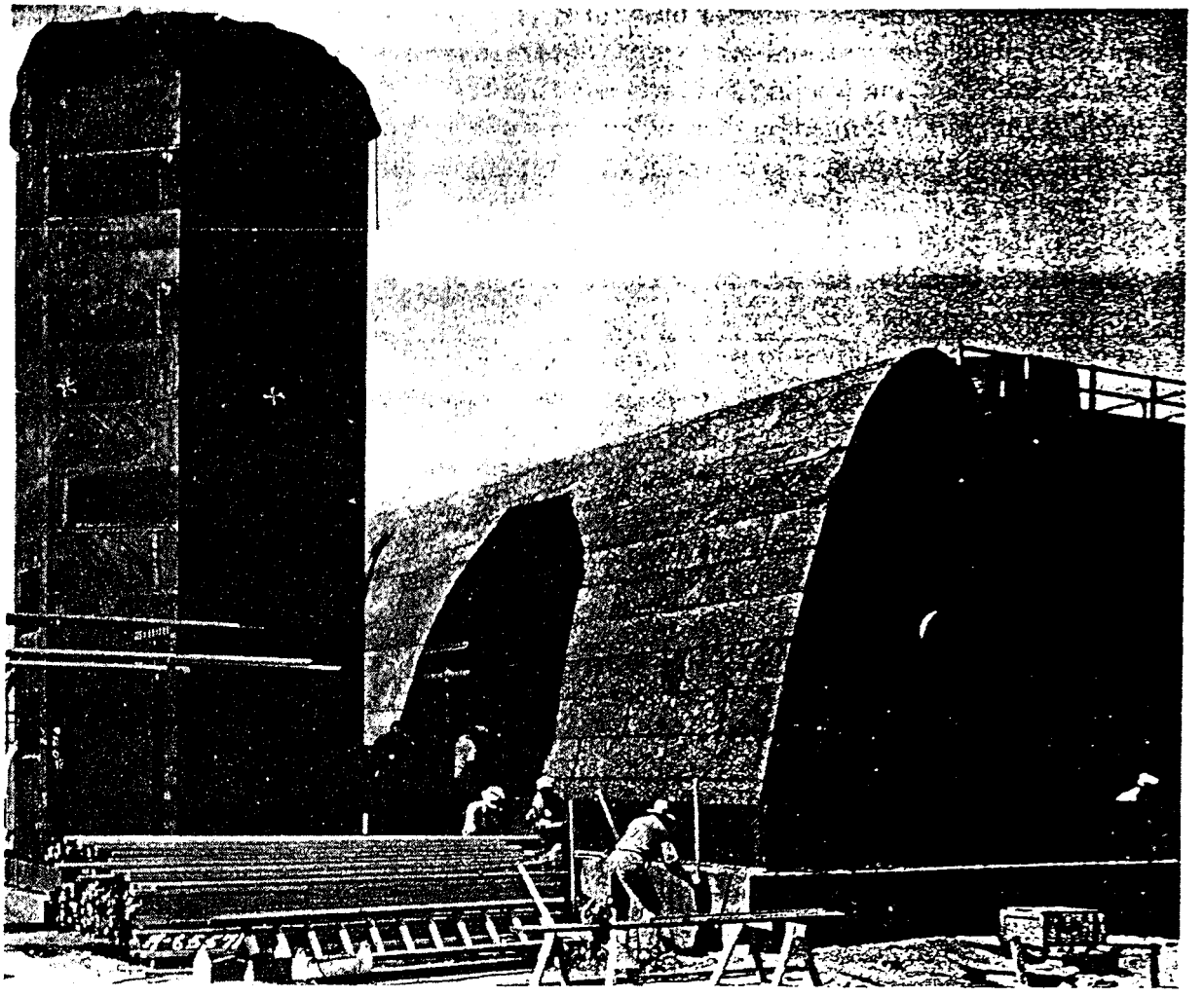

Fig. 5.5. Unit for production of phosphoric acid. The right-hand structure is built completely of electric-furnace graphite, whereas the tower at the left is assembled of amorphous carbon blocks. *(Union Carbide Corp., Carbon Products Div.)*

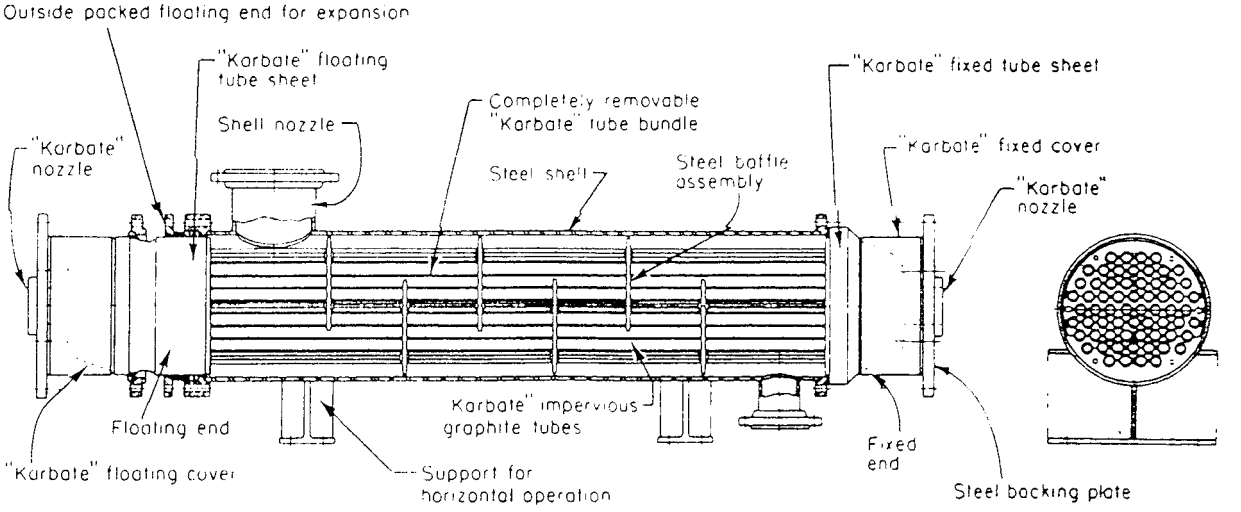

Fig. 5.6. Sectional view, impervious graphite shell-and-tube exchanger, single-tube pass. *(Union Carbide Corp., Carbon Products Div.)*

metallurgical uses in the bosh zones of blast furnaces, cupola linings, runout troughs, molds, dies, and crucibles. *Electrical* and *mechanical* uses are in brushes, resistors, contacts, electron-tube parts, seal rings, and welding and projector carbons.

Pyrolytic graphite is formed by thermal cracking of a hydrocarbon gas, such as methane, and deposition on a substrate. The deposit is very anisotropic; that is, the thermal conductivity is not the same in all directions. It equals copper in the xy plane and aluminum oxide in the z direction. It can be deposited at near theoretical density and in extremely pure form, and its uses include crucibles, fixtures for processing metals and alloys such as germanium and gallium arsenide, rocket nozzles, and coatings for nuclear fuel particles.

Carbon fibers have stiffness-to-weight and strength-to-weight ratios exceeding those of common structural materials. Fiber prices have decreased from $1200 per kilogram in 1965 to less than $50 per kilogram in 1981. Synthetic resin composites are used in aerospace and space structures, where weight savings are important, and in high-performance sporting goods. All-carbon composites, made by pyrolyzing the resin matrix, are used in aerospace applications and are being investigated as friction materials in brakes.

Extremely *high purity graphite* is used in many nuclear reactors as a moderator and reflector. The moderator holds the nuclear fuel in position and "moderates" or slows down the fast-moving neutrons to speeds at which they can be captured, thus enabling the chain reaction to continue. The reflector surrounds the moderator and scatters the escaping neutrons back into the core. In some reactors, graphite is also used as a matrix in which to disperse and contain the nuclear fuel. High-purity graphite is also widely used in the semiconductor industry for single-crystal growth and chamber heaters, and in epitaxial reactors as susceptors.

MANUFACTURE.[15] Manufactured graphite is made electrically from retort or petroleum coke, in line with the flowchart depicted in Fig. 5.7. The reaction for this allotropic change is essentially

$$C(amorph) \rightarrow C(graphite) \qquad \Delta H = -10.5 \text{ kJ}$$

The procedure involved in commercializing these reactions, as charted in Fig. 8.7, may be summarized for electrodes and other graphite articles.

Coke (petroleum or coal) is selected and shipped to the graphite plant.

Carbon material is calcined (1250°C) to volatilize impurities.

Calcined materials are carefully analyzed.

Calcined materials are ground, screened, weighed, mixed with binder, formed by molding or extrusion into green electrodes, and arranged in the furnace.

Green electrodes are baked at 900°C to carbonize the binder and furnish amorphous electrodes.

Amorphous electrodes are graphitized in the electric furnace at high temperature (2700°C).

Graphite is shipped to industrial demands, and the scrap is powdered.

In manufacturing graphite the furnace used consists essentially of a core of the coke that is being graphitized, surrounded by a heavy layer of sand, coke, and sawdust as insulation.

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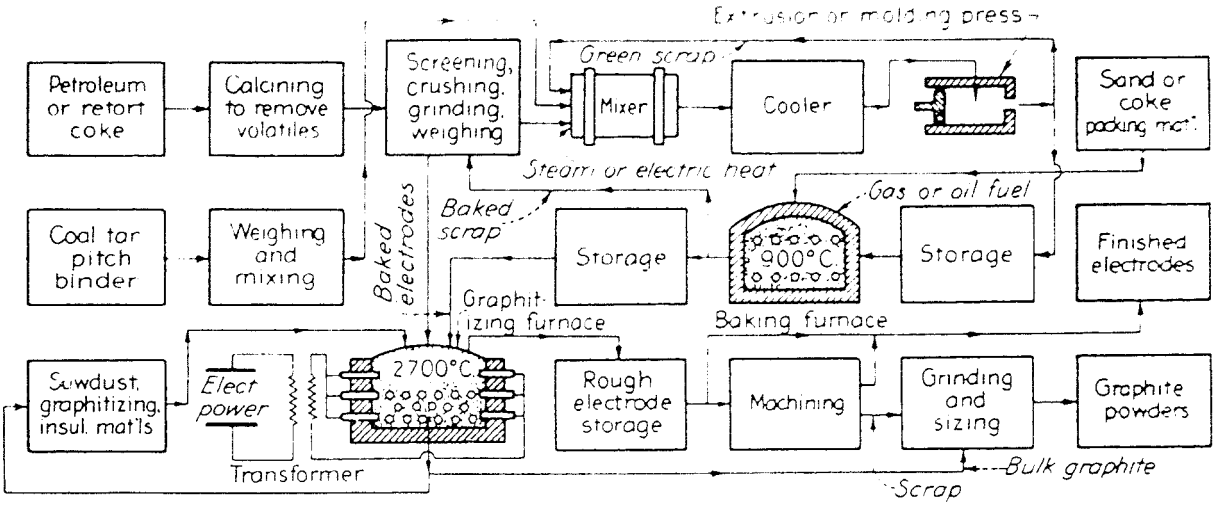
[15]ECT, 3d ed., vol. 4, 1978, p. 570; *Industrial Graphite Engineering Handbook*, Union Carbide Corp., Carbon Products Division, New York, 1970.



In order to produce 1 t of finished graphite, the following materials and utilities are required

Binder (pitch)	252 kg
Coke	1.5 t
Electricity	24,000–40,000 MJ

Fig. 5.7. Flowchart for the manufacture of artificial graphite electrodes and powders.

The floor and ends of the furnace are built mainly of concrete, with cooling coils at the ends to reduce the temperature of the electrodes in contact with air, to prevent them from burning. The side walls, built of loose blocks and plates, are torn down after each run. The average charge is from 23,000 to 90,000 kg of material. The resistance of the charge makes possible a temperature of up to 3000°C. As the coke graphitizes, the voltage, because of lowered resistance, drops from 200 to 40 V. The high temperature employed volatilizes most of the metallic impurities. A complete cycle of the furnace consists of loading, 1 day; power on, 4 to 5 days; cooling, about 14 days; unloading, 2 days. Thus about 22 days are required from charge to charge. After cooling, the furnace is torn down and the graphitized carbon taken out. The insulating sand, coke, and any silicon carbide contamination are used over again. Recently, direct current has also been employed,[16] and at least one company conducts the graphitizing in a double-row countercurrent graphitizing furnace. The opposite row, after graphitizing, imparts its heat to the incoming carbon to be graphitized. To operate such a furnace, all blocks to be graphitized must be of about the same size.

In the manufacture of amorphous carbon electrodes,[17] the petroleum coke or anthracite coal used is crushed and hot-mixed with a pitch binder (Fig. 5.8). The resulting soft mass is either extruded or molded to the finished electrode shape. These green electrodes are then baked at about 950°C in either a gas-fired furnace or an electric furnace. After cooling and removal from the furnace, they are turned down and threaded on a lathe in the same manner as that used for graphite electrodes. A similar process is involved in making brushes for motors; the carbon is formed into small plates, which are then cut to the necessary shape for making the brushes. Graphite electrodes have less electrical resistance and consequently can

[16]Olson and Price, A D-C Graphitizing Furnace, *Elec. Eng. (N.Y.)* 82 260–263 (1963); Dow Changes to DC for Graphitizing, *Chem. Eng. News* 40 (2) 46 (1963).

[17]Detailed flowcharts for both carbon and graphite electrodes are given by Mantell, *Electrochemical Engineering*, McGraw-Hill, New York, 1960, pp. 380 and 623.

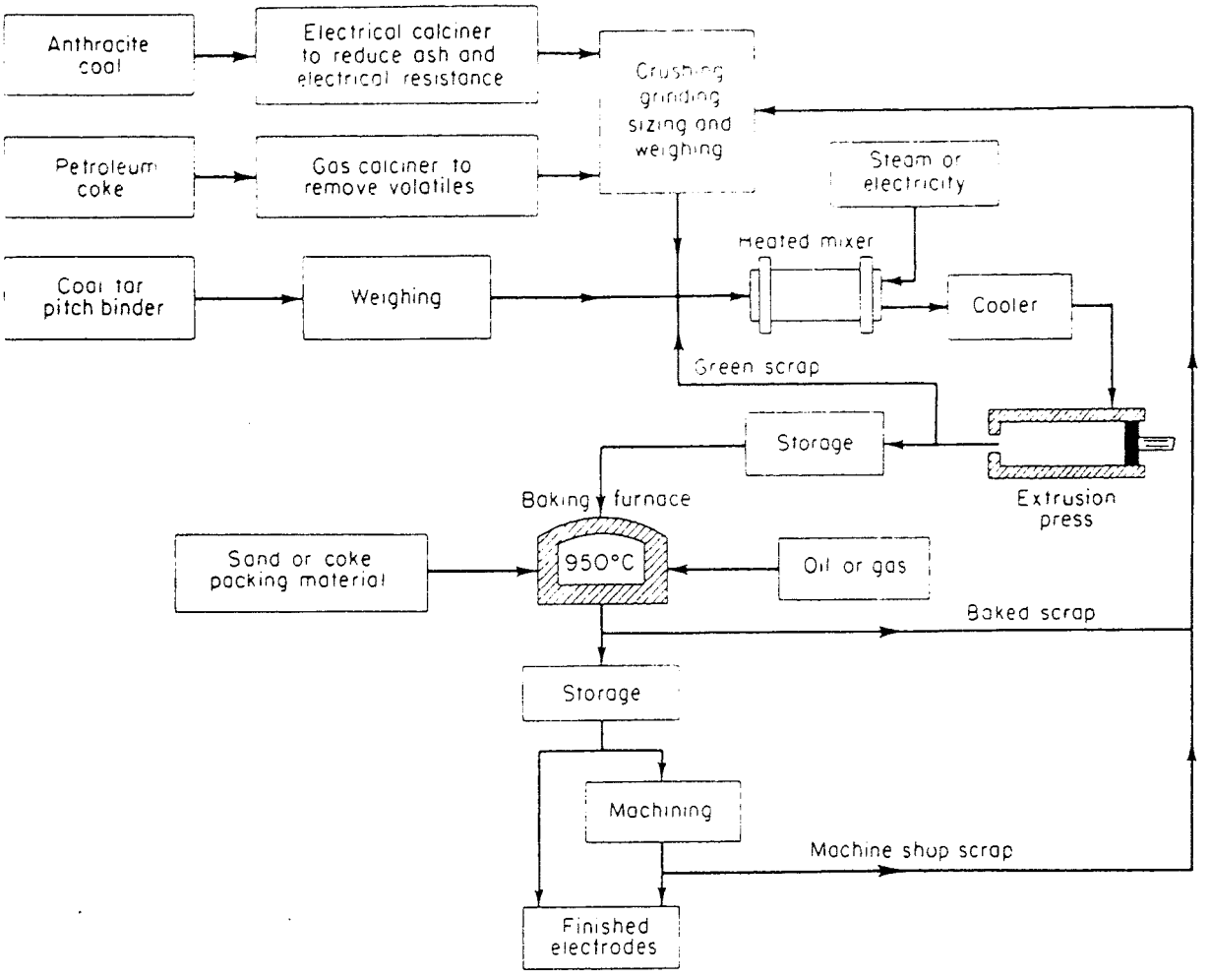


Fig. 5.8. Flowchart for manufacture of amorphous-carbon electrodes.

conduct more current per cross section, but they cost more than the usual amorphous carbon electrodes.

Pyrolytic graphite[18] is produced by the thermal cracking of hydrocarbons such as methane, propane, and acetylene at reduced pressures or diluted by an inert carrier gas. Structural shapes or flat plates up to about 2 cm in thickness can be formed by passing the gas over a heated mandrel of the desired shape. Small particles, e.g., nuclear fuel particles, are coated in a heated, fluidized bed in which the hydrocarbon-inert carrier gas mixture is used to fluidize the bed. The graphite structure, hence the properties, can be varied widely by changing the operating conditions.

Carbon fibers[19] are made by the pyrolysis of organic precursor fibers, usually rayon, polyacrylonitrile (PAN), or pitch. Fibers carbonized at 1300 to 1600°C have a modulus typically

[18]Smith and Leeds, "Pyrolytic Graphite" in *Modern Materials: Advances in Development and Applications*, Gonser (ed.), vol. 7, Academic, New York, 1970, pp. 139–221; Bokros, "Deposition, Structure, and Properties of Pyrolytic Carbon" in *Chemistry and Physics of Carbon*, Walker (ed.), vol. 5, Marcel Dekker, New York, 1969, pp. 1–118.

[19]ECT, 3d ed., vol. 4, 1978, p. 622; a flowchart for a PAN process is given in Iammartino, Graphite Fibers Forge Ahead, *Chem. Eng.* 79 (3) 30 (1972); Carbon Fibers Take Off, *Chem. Business* p. 41, July 27, 1981.

of 230 GPa (33 million psi) and a tensile strength of 2.1 to 2.8 Gpa (300 to 400,000 psi). Graphitization to 2800°C increases the modulus by a factor of 2 or 3; the strength may either increase or decrease, depending on the fiber type.

INDUSTRIAL DIAMONDS

Because diamond is the hardest of all known substances, it has great industrial importance in cutting, shaping, and polishing hard substances. Diamond is used extensively for grinding tungsten carbide tooling, glass, and nonferrous metals, and for sawing and drilling concrete and stone. Tungsten-filament wire for electric lights and millions of miles of other kinds of wire are drawn through diamond dies. The United States is the largest consumer of industrial diamonds in the world. The world production of industrial diamonds is of the order of 90 percent of the total diamond production in weight.

According to U.S. government statistics, in 1979 the United States imported about 11.4×10^6 carats (a carat is 200 mg) of industrial diamond valued at about $79 million. The U.S. production of synthetic industrial diamond was 50×10^6 carats in 1980. Natural diamond usage has remained fairly static, while synthetic has shown continuing steady growth because it can be precisely tailored to specific needs.

Three natural types are employed: (1) *crystalline* and cleavable diamonds, more or less off-grade and off-color; (2) *bort*, translucent to opaque, gray or dark brown, with a radiated or confused crystalline structure; and (3) *carbonado*, frequently known as *black diamond* or *carbon*, which occurs in an opaque, tough, crystalline aggregate without cleavage. Bort is the most widely used of industrial diamond stones, and most of it comes from Africa. Synthetic diamond has become the standard of performance for grinding wheels, saws, and drills, and is a major factor in the economy of the industry. Industrial diamonds are used extensively in the grinding of shaped carbide or ceramic tips for turning and boring tools. Bonded-diamond wheels for grinding hard, abrasive materials such as cemented carbide tools, ceramics, and glass are made from synthesized diamond crystals or crushed bort, held by a matrix of resin, vitreous material, or sintered metal. Tools set with industrial diamond are a practical necessity in truing and dressing worn abrasive wheels in all industries where precision grinding is performed. Diamond lathe tools, because of the hardness and high heat conductivity of diamond, allow greatly increased machining speeds in turning nonferrous metal parts to close tolerances and fine finishes. Since the continuous drawing of wire through reduction dies causes much wear, dies for accurate wire drawing are made of diamonds. Such dies are generally made from fine-quality single-crystal stones with an appropriate hole drilled through them. Recently, successful wire-drawing dies have been made from diamond compacts which consist of fine diamond crystals thoroughly bonded together. The holes are started by using sharp diamond points, or by a fine laser beam, and are finished by lapping with fine diamond dust. When worn, dies must be redressed to the next larger wire size. Diamond dies used for drawing ferrous wire were formerly smaller than 2.5 mm in diameter, but now are replacing tungsten carbide wire-drawing dies in sizes up to 4.6 mm in diameter.[20] Bore sizes up to 7.6 mm have been made to draw nonferrous wire. Many companies producing copper wire have shifted to diamond compacts for dies replacing tungsten carbide. Diamond bits for drilling

[20]Rose, How Far Can Synthetic Diamond Wiredrawing Dies Go? *Wire J.* 14 54–59 (1981); Sarver, Drawing Large Diameter Wire with Diamond Dies. *Wire Tech.* 5 (4) 25 (1977).

through hard rock formations for oil, gas, or water, for boring blast-charge holes in mines and quarries, and for drilling holes in and taking cores from concrete structures are set with small whole diamonds in a sintered metal bond. Here the diamonds do the actual work, the steel heads simply serving to hold them in the cutting position. Diamond drill crowns allow actual cores of rock to be taken from great depths and examined to yield information on what minerals or deposits are present. The increasing trend toward automation is causing the increase in domestic consumption of industrial diamonds to be greater than that of other abrasives.

In 1957 General Electric Co. commercially introduced synthetic diamond grit for resin-bonded grinding wheels, the production of which is based on a process discovered by scientists in its research laboratory in 1954.[21] The same basic process is used currently in factories in South Africa, Ireland, Sweden, Japan, and Russia.

The process requires pressures and temperatures in the region of thermodynamic stability for diamond (versus graphite, see Fig. 5.9) and a molten catalyst-solvent metal consisting of a group VIII metal or alloy. Special ultra-high-pressure apparatus is used, the moving members of which are forced together by large hydraulic presses. One of the 900-t hydraulic presses used at the General Electric Research and Development Center is shown in Fig. 5.10. It is a batch process requiring a period of a number of minutes. Different types and sizes of diamond particles, or crystals, require different conditions of pressure, temperature, catalyst-solvent, and reaction time. The crude diamonds are cleaned and graded by size and shape. Many different types are now currently available, ranging from the finest polishing powders up to 20-mesh blocky crystals, which yield excellent service in saws and drills for ceramic, stone, and concrete cutting.

Very fine diamond polishing powders can be made directly from certain graphites by shock-compression processes.[22] A shock wave of the order of 300 to 1200 MPa intensity and 10^{-6} s duration is passed through the graphite. In the DuPont process the graphite particles are dispersed in a metal matrix, which helps to transmit the pressure wave and to thermally quench the extremely hot carbon components of the system immediately after compression. The thermal quench helps prevent graphitization of the diamond formed during the compression. The metal is removed by acids, and the extraneous graphite by selective oxidation processes. This process is not a significant factor in the synthetic diamond industry. It is not run continuously, and as fines are readily available at a low price, it probably is not run very often.

Techniques have been developed for bonding diamond crystals into strong, relatively tough compacts. These compacts are either used for drill bits or cemented to a tungsten carbide substrate to form tool blanks. The compacts have large, sharp cutting edges that remain sharp throughout their life because new diamond crystals are continuously exposed during use. The blanks have the hardness and abrasion resistance of diamond and the impact resistance of tungsten carbide.

The diamondlike abrasive material, cubic boron nitride,[23] is synthesized, marketed, and used commercially. It is made from hexagonal boron nitride at pressures and temperatures

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[21]Bundy, Hall, Strong, and Wentorf, Jr., *Nature* 176 51 (1955).

[22]DeCarli and Jamieson, *Science* 133, 182 (1961); Mears and Bowman, paper presented at Industrial Diamond Association of America, Technical Session, Mar. 7, 1966, Boca Raton, Fla.; E. I. DuPont de Nemours & Co. U.S. Patent 3,401,019 (1966); Gladysz, Squeezing the Transition State, *CHEMTECH* 9 (6) 372 (1979).

[23]Wentorf, *J. Chem. Phys.* 26 956 (1957).

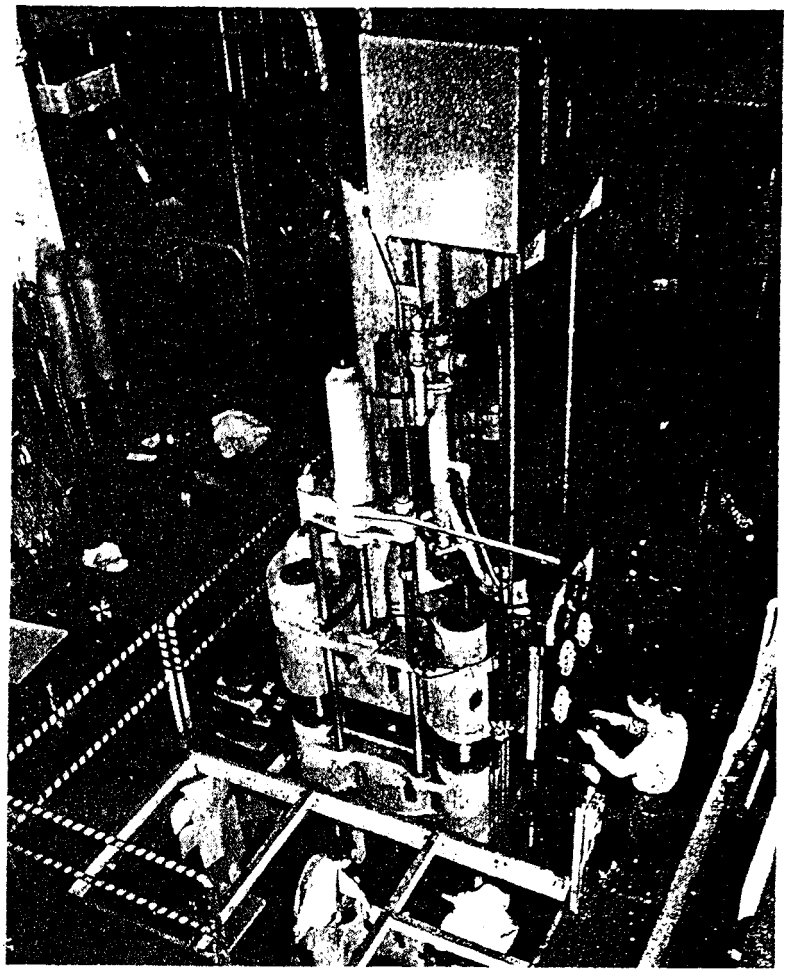

Fig. 5.10. A 900-t hydraulic press used to provide the squeezing force on the belt superpressure apparatus for synthetic diamonds. *(General Electric Co.)*

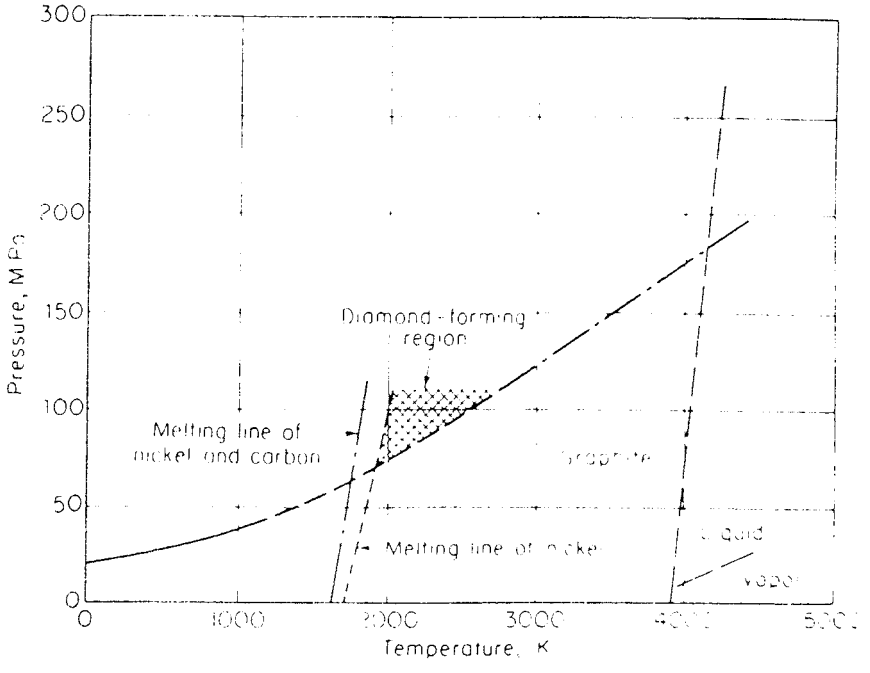

Fig. 5.9. Diamond-forming region for nickel-carbon system. *(ECT, 3d ed., vol. 4, p. 678, 1978.)*

similar to those used in diamond synthesis but with different catalyst-solvent materials. Compacts of cubic boron nitride are also made. Cubic boron nitride abrasive grain is particularly effective in grinding hard ferrous metals with which diamond tends to react. In general, diamond abrasive works best on hard nonmetallic materials, while cubic boron nitride abrasive does best on hard metallic materials.

Gem-quality diamonds can be grown in the laboratory,[24] but the process is slow and expensive and is not considered economically feasible in the usual market. However, these diamonds have the highest thermal conductivity of any known material, more than matching that of type II natural diamond crystals,[25] and they may become useful as heat sinks for high-power-density microelectric solid-state devices and for high-intensity laser beam windows.

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[24]Wentorf, *J. Chem. Phys.*, 75 1833 (1971).

[25]Strong and Chrenko, *J. Chem. Phys.* 75 1838 (1971).

Chapter 6

Ceramic Industries

The traditional ceramic industries, sometimes referred to as the *clay products* or *silicate industries*, have as their finished materials a variety of products that are essentially silicates.[1] In recent years new products have been developed as a result of the demand for materials that withstand higher temperatures, resist greater pressures, have superior mechanical properties, possess special electrical characteristics, or can protect against corrosive chemicals. The following types of products are considered in this chapter:

1. ***Whitewares.*** China, earthenware, pottery, porcelain, stoneware, and vitreous ware.
2. ***Structural clay products.*** Building brick, face brick, terra-cotta, sewer pipe, and drain tile.
3. ***Refractories.*** Firebricks; silica, chromite, magnesite, magnesite-chromite brick; silicon carbide and zirconia refractories; aluminum silicate and alumina products.
4. ***Specialized ceramic products.***
5. ***Enamels and enameled metal.***

The glass, cement, and artificial-abrasives industries are dealt with in separate chapters, since the emphasis of this book is on manufacturing procedures peculiar to the major chemical process industries.[2]

HISTORICAL. Pottery making is one of the most ancient of human industries. Burnt clayware has been found dating from about 15,000 B.C. and was well developed in Egypt 10 centuries later. Museums contain, as a record of culture, clay products created independently by various races. Demands for superior materials have produced a broader spectrum of systems; greater emphasis has been placed on the cross-fertilization of *silicate chemistry* with metallurgy and solid-state physics, coupled with many computer-controlled processes and advancing automation, which characterize modern methods of fabrication. Recently, new processes have been under development for brickmaking from inorganic wastes such as fly ash from power plants, foundry sand, mine tailings, furnace slag, and a large variety of other materials.

[1] Kingery, *Introduction to Ceramics*, 2d ed., Wiley, New York, 1976.

[2] ECT, 3d ed., vol. 5, 1979, p. 234: "Ceramics (plural noun) comprise all engineering materials or products that are chemically inorganic, except metals and metal alloys, and are usually rendered serviceable through high temperature processing. The word *ceramic* may be used as a singular noun but is more often used as an adjective meaning inorganic, nonmetallic. A primary difference between ceramics and metals is the nature of their chemical bonding. The difference is responsible for characteristic properties and behavior of ceramics. Composites such as ceramics-metal combinations and others involving organic materials are often included as ceramic materials."

that lie in mammoth piles throughout the country.[3] Other new developments are appearing in the patent literature.[4]

USES AND ECONOMICS. Inasmuch as sales data on whitewares are not usually available, and because many ceramic products are used as components of finished materials classified in other categories, it is difficult to determine their sales volume. However, an extensive effort at studying this industry is made each year by the Bureau of Mines. The economic statistics are summarized in Table 6.1. Clays were produced in 46 states and Puerto Rico in 1979. The states leading in clay output in 1979 were Georgia, 7.5×10^6 t, Texas, 3.5×10^6 t, and Ohio, 3.7×10^6 t.[4a] Georgia also leads in total value of clay output with $437.6 million. Sixty percent of all clay produced is consumed in the manufacture of heavy-clay construction products. Of these products, building brick, sewer pipe, and drain tile account for 38 percent of the total clay usage, portland cement accounts for 19 percent, and lightweight aggregate accounts for 10 percent. As shown in Table 6.1, the value of construction products was over $1061 million in 1980. Refractories use large quantities of clays, and usage is increasing primarily because of the use of plastic, ramming, and castable mixes. Clays are used as fillers in many products such as paper, rubber, plastics, paint, and fertilizers. Fuller's earth is the principal clay used in adsorbent applications. Other important uses include drilling mud, floor and wall tile, pelletizing iron ore, and pottery.

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[3]New Processes Turn Wastes into Bricks, *Chem. Eng. News* 49 (38) 49 (1971).

[4]Angstadt and Bell, Production of Alumina and Portland Cement from Clay and Limestone, U.S. Patent 3,642,437, Feb. 15, 1972; Burk et al., Alumina Extraction from Aluminosilicate Ores and Potassium Sulfate Ores, U.S. Patent 3,652,208, Mar. 28, 1972; Huska et al., Method and Apparatus for Converting Aluminum Nitrate Solution to Alpha Alumina, U.S. Patent 3,647,373, Mar. 7, 1972.

[4a]t = 1000 kg.

Table 6.1 Clays and Clay Products Statistics in the United States (thousands of metric tons and thousands of dollars)

	1976	1978	1979	1980	1981
Domestic Clays Sold or Used by Producers					
Quantity	48,355	51,651	49,712	43,350	40,341
Value	579,170	717,274	846,089	898,947	988,845
Exports					
Quantity	2,328	2,422	2,914	2,922	2,864
Value	160,790	194,914	243,722	263,147	292,914
Imports for Consumption					
Quantity	33	23	46	31	30
Value	1,917	2,082	3,972	6,688	7,595
Clay Refractories Shipments					
Value	465,442	497,567	580,257	557,286	609,949
Clay Construction Products Shipments					
Value	993,508	1,158,278	1,179,058	1,061,507	971,824

SOURCE: *Minerals Yearbook 1981*, vol. 1, U.S. Dept. of the Interior, 1982, p. 223.

BASIC RAW MATERIALS[5]

The three main raw materials used in making classic, or "triaxial," ceramic products are clay, feldspar, and sand. Clays are more-or-less impure hydrated aluminum silicates that have resulted from the weathering of igneous rocks in which feldspar was a noteworthy original mineral. The reaction may be expressed:

$$\underset{\text{Potash feldspar}}{K_2O \cdot Al_2O_3 \cdot 6SiO_2} + CO_2 + 2H_2O \rightarrow K_2CO_3 + \underset{\text{Kaolinite}}{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O} + \underset{\text{Silica}}{4SiO_2}$$

There are a number of mineral species called *clay minerals*, which contain mainly mixtures of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), montmorillonite [$(Mg, Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$], and illite ($K_2O$, MgO, Al_2O_3, SiO_2, H_2O, all in variable amounts). From a ceramic viewpoint clays are plastic and moldable when sufficiently finely pulverized and wet, rigid when dry, and vitreous when fired at a suitably high temperature. Upon these properties depend the manufacturing procedures.

Accompanying clay minerals in the clays of commerce are varying amounts of feldspar, quartz, and other impurities such as oxides of iron. In nearly all the clays used in the ceramic industry, the basic clay mineral is kaolinite, although bentonite clays based on montmorillonite are used to some extent where very high plasticity is desired. This property of plasticity, or workability, is influenced most by the physical condition of the clay and varies greatly among different types of clays. Clays are chosen for the particular properties desired and are frequently blended to give the most favorable result. Clays vary so much in their physical properties and in the impurities present that it is frequently necessary to upgrade them by the *beneficiation* procedure. Figure 6.1 shows the steps necessary for such a procedure, wherein sand and mica are removed. Almost all the steps in this flowchart apply to physical changes, or *unit operations*, such as size separation by screening or selective settling, filtration, and drying. However, the colloidal properties are controlled by appropriate additives such as sodium silicate and alum. Beneficiation processes also include froth flotation.[6] Chemical purification is used for high-purity materials such as alumina and titania.

There are three common types of *feldspar*, potash ($K_2O \cdot Al_2O_3 \cdot SiO_2$), soda ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$), and lime ($CaO \cdot Al_2O_3 \cdot 6SiO_2$), all of which are used in ceramic products to some extent. Feldspar is of great importance as a fluxing constituent in ceramic formulas. It may exist in the clay as mined, or it may be added as needed. Half of the feldspar used in the United States comes from North Carolina. The third main ceramic constituent is sand or *flint*. Its essential properties for the ceramic industries are summarized, along with the similar characteristics of clay and feldspar, in Table 6.2. For light-colored ceramic products, sand with a low iron content should be chosen.

[5]ECT, 3d ed., vol. 5, 1979, p. 237 presents a detailed discussion of raw materials. Nepheline syenite, $(Na,K)_2Al_2Si_2O_8$; a quartz-free igneous rock, is used extensively in whitewares; it is a more active flux than feldspar; Worrall, *Clays and Ceramic Raw Materials*, Halsted, New York, 1975.

[6]See Perry, pp. 21-65 to 21-69, for flotation.

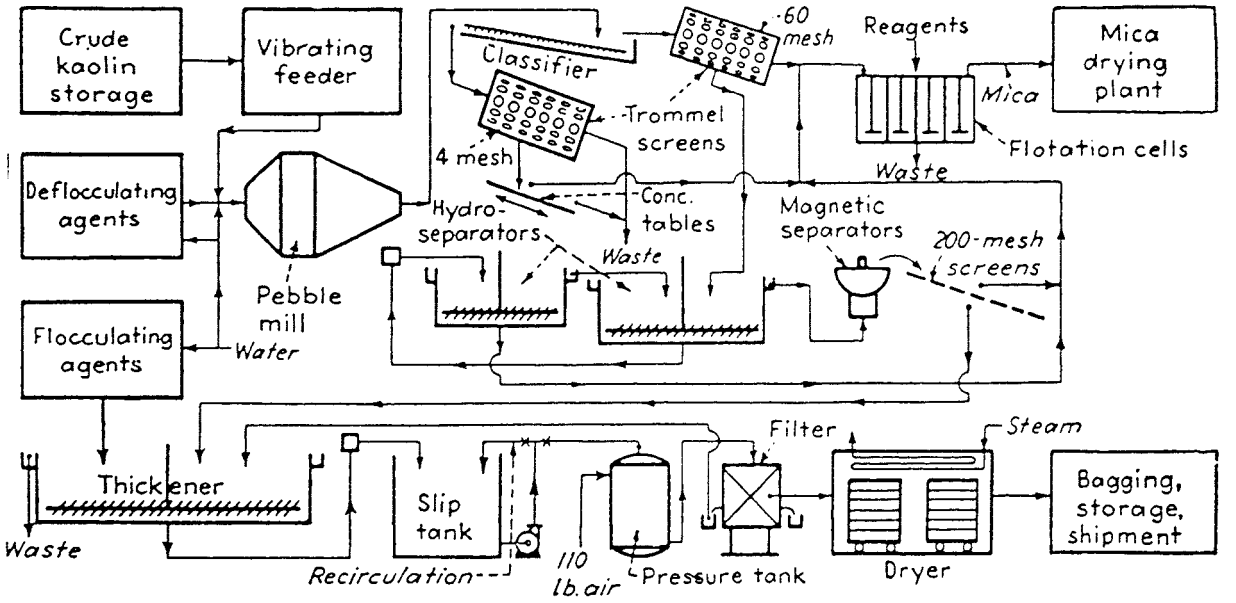

Fig. 6.1. China-clay beneficiation. NOTE: Quantities cannot be given since clay recovery varies from 8 to 18 percent depending on the crude clay used. The plant shown here is designed for 30-t/day output, regardless of crude clay variations. *(Harris Clay Co.)*

In addition to the three principal raw materials, a wide variety of other minerals, salts, and oxides is used as fluxing agents and special refractory ingredients. Some of the more *common fluxing agents* that lower vitrification temperature, melting temperature, or reaction temperature are:

Borax ($Na_2B_4O_7 \cdot 10H_2O$)
Boric acid (H_3BO_3)
Soda ash (Na_2CO_3)
Sodium nitrate ($NaNO_3$)
Pearl ash (K_2CO_3)
Nepheline syenite [$(Na,K)_2Al_2Si_2O_8$]
Calcined bones
Apatite [$Ca_5(F,Cl,OH)(PO_4)_3$]
Fluorspar (CaF_2)
Cryolite (Na_3AlF_6)
Iron oxides
Antimony oxides
Lead oxides
Lithium minerals
Barium minerals

Some of the more common *special refractory ingredients* are

Alumina (Al_2O_3)
Olivine [$(FeO,MgO)_2SiO_2$]
Chromite ($FeO \cdot Cr_2O_3$)
Magnesite ($MgCO_3$)
Lime (CaO) and limestone ($CaCO_3$)
Zirconia (ZrO_2)
Titania (TiO_2)
Hydrous magnesium silicates, e.g., talc ($3MgO \cdot 4SiO_2 \cdot H_2O$)
Aluminum silicates ($Al_2O_3 \cdot SiO_2$) (kyanite, sillimanite, andalusite)
Dumortierite ($8Al_2O_3 \cdot B_2O_3 \cdot 6SiO_2 \cdot H_2O$)
Carborundum (SiC)
Mullite ($3Al_2O_3 \cdot 2SiO_2$)
Dolomite [$CaMg(CO_3)_2$]
Thoria (ThO_2)

Many other raw materials are used in various combinations; at least 450 have been classified.[7]

[7]Raw Materials, *Ceram. Age.* **79** (10) 21 (1963).

***Table* 6.2** Basic Raw Materials for Ceramics

	Kaolinite	Feldspar	Sand or Flint
Formula	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	SiO_2
Plasticity	Plastic	Nonplastic	Nonplastic
Fusibility	Refractory*	Easily fusible binder	Refractory*
Melting point	1785°C	1150°C	1710°C
Shrinkage on burning	Much shrinkage	Fuses	No shrinkage

*Infusable at highest temperature of coal fire (1400°C).

CHEMICAL CONVERSIONS, INCLUDING BASIC CERAMIC CHEMISTRY

All ceramic products are made by combining various amounts of the foregoing raw materials, shaping, and heating to firing temperatures. These temperatures may be as low as 700°C for some overglazes or as high as 2000°C for many vitrifications. Such temperatures cause a number of reactions, which are the chemical bases for the *chemical conversions:*

1. Dehydration, or "chemical water smoking," at 150 to 650°C
2. Calcination, e.g., of $CaCO_3$ at 600 to 900°C
3. Oxidation of ferrous iron and organic matter at 350 to 900°C
4. Silicate formation at 900°C and higher

Some of the initial chemical changes are relatively simple, such as calcination of $CaCO_3$ and the dehydrations and decompositions of kaolinite. Other reactions, such as silicate formations, are quite complex and change with the temperature and constituent ratios as depicted by Fig. 6.2. Phase-rule[8] studies have been of importance in interpreting empirical observations in the ceramic industries and in making predictions for improvements. For instance, the data in Fig. 6.2 on the $Al_2O_3 \cdot SiO_2$ system have led to the important development of processes for mullite refractories. This diagram shows that any percentage of liquefaction can be obtained, dependent on a definite temperature, except at the monovariant points. Thus, if the progressive melting is kept from going too far by controlling the rise in temperature, sufficient solid skeletal material will remain to hold the hot mass together. This $Al_2O_3 \cdot SiO_2$ diagram shows that mullite is the only stable compound of alumina and silica at high temperatures.

Ceramic products are all more or less refractory, i.e., resistant to heat, and the degree of refractoriness of a given product is determined by the relative quantities of refractory oxides and fluxing oxides. The principal refractory oxides are SiO_2, Al_2O_3, CaO, and MgO, with ZrO_2, TiO_2, Cr_2O_3, and BeO used less commonly. The principal fluxing oxides are Na_2O, K_2O, B_2O_3, and SnO_2, with fluorides also used as fluxes in certain compositions.

The common ingredient of all ceramic products is clay (kaolinite, usually), and therefore the chemical reactions which occur on heating clay are quite important. The first effect of

[8]Kingery, op. cit., contains detailed discussion, tables of physical properties, and other phase diagrams; *Phase Diagrams for Ceramists*, American Ceramic Society, Columbus, Ohio, vol. 1, 1964; vol. 2, 1969; vol. 3, 1975; vol. 4, 1981.

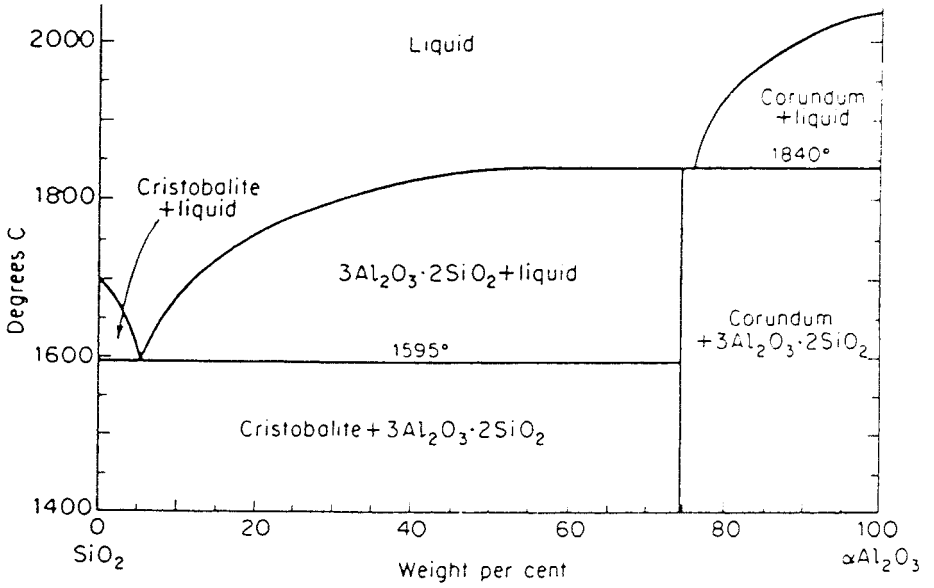

Fig. 6.2. Phase diagram of the system $\alpha Al_2O_3 \cdot SiO_2$. Mullite is $3Al_2O_3 \cdot 2SiO_2$, cristobalite is SiO_2, and corundum is Al_2O_3.

the heat is to drive off the water of hydration; this occurs at about 600 to 650°C and absorbs much heat, leaving an amorphous mixture of alumina and silica, as shown by x-ray studies.

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 + 2SiO_2 + 2H_2O$$

In fact, a large proportion of the alumina can be extracted with hydrochloric acid at this stage. As heating is continued, the amorphous alumina changes quite sharply at 940°C to a crystalline form of alumina, γ-alumina, with the evolution of considerable heat. At a slightly higher temperature, beginning at about 1000°C, the alumina and silica combine to form mullite ($3Al_2O_3 \cdot 2SiO_2$). At a still higher temperature, the remaining silica is converted into crystalline cristobalite. Therefore the fundamental overall reaction in the heating of clay is as follows:

$$\underset{\text{Kaolinite}}{3(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)} \rightarrow \underset{\text{Mullite}}{3Al_2O_3 \cdot 2SiO_2} + \underset{\text{Cristobalite}}{4SiO_2} + 6H_2O$$

The equilibrium state of Al_2O_3–SiO_2 mixtures as a function of temperature is summarized in the phase-equilibrium diagram of this system shown in Fig. 6.2. The presence of fluxes tends to lower the temperature of formation of mullite and speeds up the approach to equilibrium.

An actual ceramic body contains many more ingredients than clay itself. Hence the chemical reactions are more involved, and there will be other chemical species besides mullite and cristobalite present in the final product. For example, various silicates and aluminates of calcium, magnesium, and possibly alkali metals may be present. However, the alkali portion of feldspar and most of the fluxing agents become part of the glassy, or vitreous, phase of the ceramic body. All ceramic bodies undergo a certain amount of vitrification, or glass formation, during heating, and the degree of vitrification depends upon the relative amounts of refractory and fluxing oxides in the composition, the temperature, and the time of heating. The vitreous phase imparts desirable properties to some ceramic bodies, e.g., by acting as a bond and imparting translucency in chinaware. Even in refractories some vitrification is desirable to act as a bond, but extensive vitrification destroys the refractory property. Thus it

is seen that any ceramic body is composed of a vitreous matrix plus crystals, of which mullite and cristobalite are two of the most important

The *degree of vitrification*, or the progressive reduction in porosity, provides the basis for a useful classification of ceramic products as follows:

1. ***Whitewares.*** Varying amounts of fluxes, heat at moderately high temperatures, varying vitrification.
2. ***Heavy-clay products.*** Abundant fluxes, heat at low temperatures, little vitrification.
3. ***Refractories.*** Few fluxes, heat at high temperatures, little vitrification.
4. ***Enamels.*** Very abundant fluxes, heat at moderate temperatures, complete vitrification.
5. ***Glass.*** Moderate fluxes, heat at high temperatures, complete vitrification (Chap. 8).

WHITEWARES

Whiteware is a generic term for ceramic products which are usually white and of fine texture. These are based on selected grades of clay bonded together with varying amounts of fluxes and heated to a moderately high temperature in a kiln (1200 to 1500°C). Because of the different amounts and kinds of fluxes, there is a corresponding variation in the degree of vitrification among whitewares, from earthenware to vitrified china. These may be broadly defined as follows:

Earthenware, sometimes called *semivitreous* dinnerware, is porous and nontranslucent with a soft glaze.

Chinaware is a vitrified translucent ware with a medium glaze which resists abrasion to a degree; it is used for nontechnical purposes.

Porcelain is a vitrified translucent ware with a hard glaze which resists abrasion to the maximum degree. It includes chemical, insulating, and dental porcelain.

Sanitary ware, formerly made from clay, was usually porous; hence a vitreous composition is presently used. Prefired and sized vitreous grog is sometimes included with the triaxial composition.

Stoneware, one of the oldest of ceramic wares, was in use long before porcelain was developed; in fact, it may be regarded as a crude porcelain not so carefully fabricated from raw material of a poorer grade.

Whiteware tiles, available in a number of special types, are generally classified as floor tiles, which are resistant to abrasion and impervious to stain penetration and may be glazed or unglazed, and as wall tiles which also have a hard, permanent surface and come in a variety of colors and textures.

MANUFACTURE OF PORCELAIN. To represent a typical manufacturing procedure in this group, porcelain as defined above is chosen. There are three lines of production: *wet-process porcelain*, used for production of fine-grained, highly glazed insulators for high-voltage service; *dry-process porcelain*, employed for rapid production of more open-textured, low-voltage pieces; and *cast porcelain*, necessary for the making of pieces too large or too intricate for the other two methods. These three processes are based on the same raw materials, the differences in manufacturing being largely in the drying and forming (shaping) steps. The

wet process is illustrated in Fig. 6.3. This flowchart may be broken down into the following sequences:

Raw materials of proper proportions and properties to furnish porcelain of the desired quality are weighted from overhead hoppers into the weighing car.

Feldspar, clays, and flint are mixed with water in the blunger (clay-water mixer) and then passed over a magnetic separator, screened, and stored.

Most of the water is removed (and wasted) in the filter press. All the air is taken out in the pug mill, assisted by a vacuum and by slicing knives. This results in denser, more uniform, and stronger porcelain.

The prepared clay is formed into blanks in a hydraulic press or by hot-pressing in suitable molds.

The blanks are preliminarily dried, trimmed, and finally completely dried, all under carefully controlled conditions.

A high surface luster is secured by glazing with selected materials.

The vitrification of the body and the glaze is carried out in tunnel kilns, with exact controls of temperature and movement.

The porcelain articles are protected by being placed in saggers[9] fitted one on top of the other in cars. This represents a one-fire process wherein body and glaze are fired simultaneously. The porcelain pieces are rigidly tested electrically and inspected.

Much tableware is manufactured by more complicated procedures than illustrated by the somewhat related porcelain product. Some objects are shaped by being thrown on the potter's wheel where skilled hands work the revolving plastic clay into the desired form; some objects are cast from the clay slip in molds of absorbent plaster of paris. After drying, they are removed and further processed. Complex shapes such as artware and laboratoryware can be produced by this method (Fig. 6.4*b*). The mass production of simple round objects, like cups,

[9]Saggers (supports) are made by mixing coarse granules obtained from grinding old saggers with new clay and water in a pug mill and discharging the doughlike mass from an extrusion machine in loaf form. These loaves are placed in a molding machine, where a box shape is imparted, and then fired. They may be used several times.

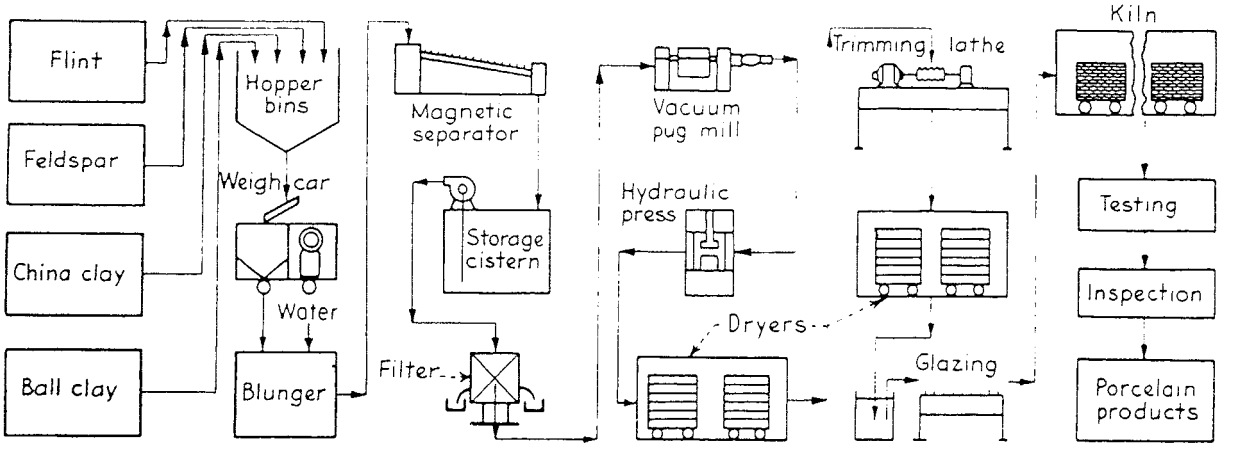

Fig. 6.3. Porcelain manufacture by the wet process of Westinghouse.

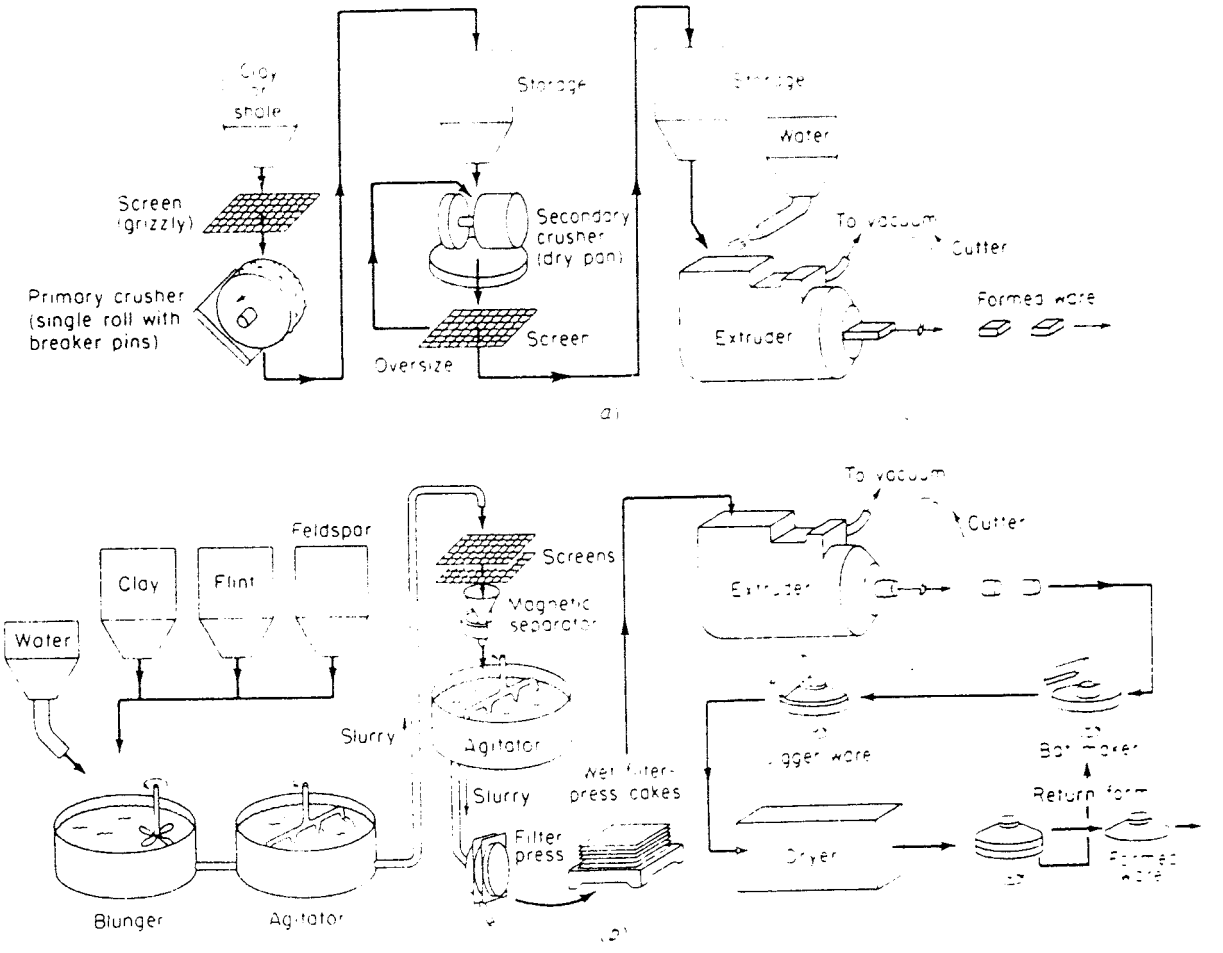

Fig. 6.4. Simplified flowcharts of forming processes (*a*) Extrusion of clay bricks. (*b*) jiggering of dinner plates. (*ECT, 3d ed., vol. 5, 1979, p. 256.*)

saucers, and plates, is carried out economically by jiggering, where the plastic clay is pressed into or on a single revolving mold, the potter often being aided in shaping the outer surface and in removing excess clay by a lever, which is lowered over the mold shaped in the profile of the object desired (Fig. 6.5*b*). Mechanized jiggers have been developed; however, high-energy mixing and rapid infrared drying are necessary in successful automation. After drying, whiteware may be fired in three ways; the common method is to fire a sufficiently high temperature to mature the body before glazing.

Glazing is important in whitewares and particularly so for tableware. A glaze is a thin coating of glass melted onto the surface of more-or-less porous ceramic ware. It contains ingredients of two distinct types in different proportions: refractory materials such as feldspar, silica, and china clay, and fluxes such as soda, potash, fluorspar, and borax. Different combinations of these materials and the different temperatures at which they are fixed give a wide range of texture and quality. Nepheline syenite permits firing at a lower temperature. The glaze must be bonded to the ware, and its coefficient of expansion must be sufficiently close to that of the ware to avoid defects such as "crazing" and "shivering." The glaze may be put on by dipping, spraying, pouring, or brushing. Decoration of such ware may be "underglaze" or "overglaze." *Glost firing* is the technical term for the firing of the glaze. Earthenware should be glazed between 1050 and 1100°C; stoneware between 1250 and 1300°C.

STRUCTURAL-CLAY PRODUCTS

Low-cost but very durable products, such as building brick, face brick, terra-cotta, sewer pipe, and drain tile, are frequently manufactured from the cheapest of common clays with or without glazing. The clays used generally carry sufficient impurities to provide the needed fluxes for binding. When the clay is glazed, as in sewer pipe or drain tile, this may be done by throwing salt ("salt glaze") upon the kiln fire. The volatilized salt reacts to form the fusible coating or glaze.

MANUFACTURE OF BUILDING BRICK. The raw materials are clays from three groups: (1) red burning clay, (2) white burning clay, and (3) buff burning clay, usually a refractory. The requirements for face-brick clay are freedom from warping, absence of soluble salts, sufficient hardness when burned at a moderate temperature, and general uniformity in color upon burning. Requirements for brick are much less stringent; red burning clay is usually used. Bricks are manufactured by one of three processes:[10] the soft-mud, the stiff-mud, or the dry-press. In the now predominant *stiff-mud* procedure, the clay is just wet enough (12 to 15 percent) to stick together when worked. This clay is forced out through an extruder (Fig. 6.5*a*). De-airing increases the workability, plasticity, and strength of undried brick by reduc-

[10]See *Chemical Process Industries*, 2d ed., for soft-mud and dry-press procedures.

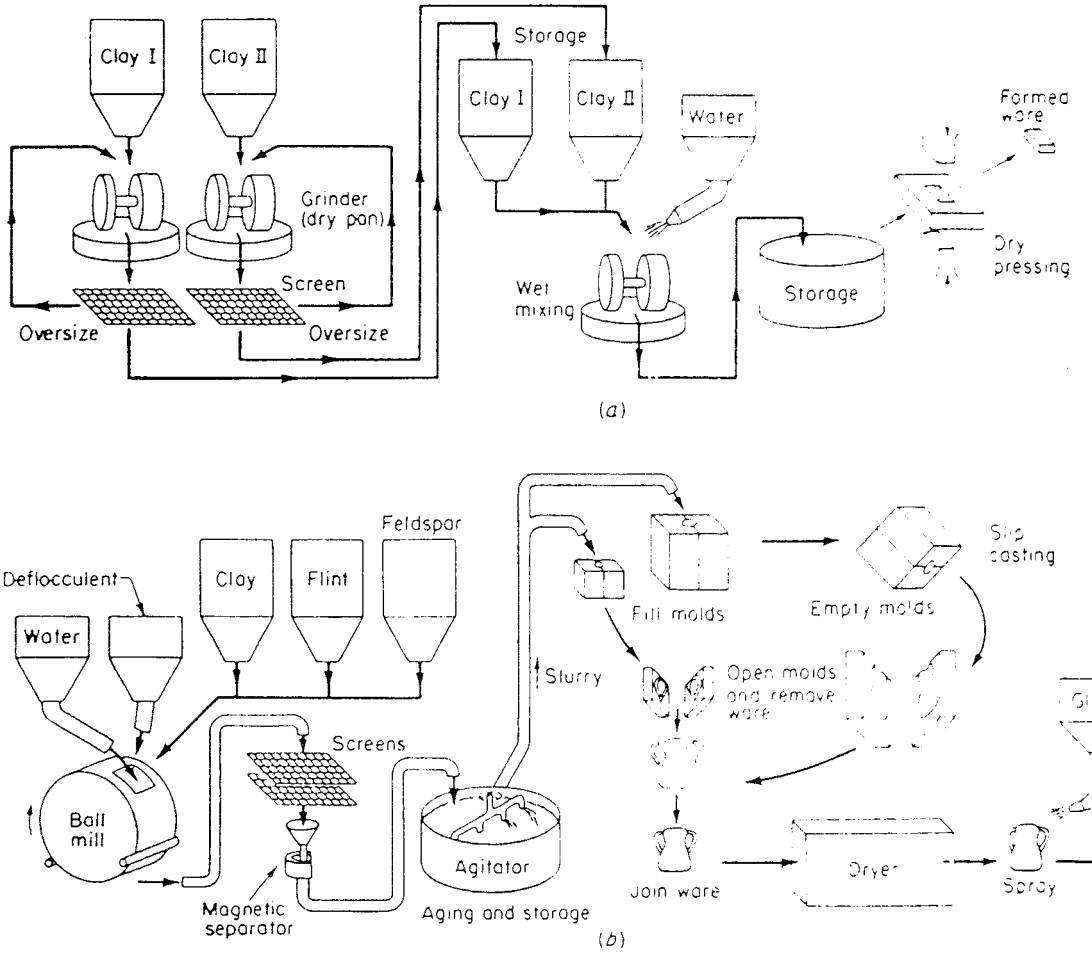

Fig. 6.5. Simplified flowcharts of forming processes. (*a*) Dry pressing of refractories. (*b*) slip-casting artware. (*ECT, 3d ed., vol. 5, 1979, p. 258.*)

ing voids. Bricks may be re-pressed to make face brick; re-pressing ensures a more uniform shape and overcomes the internal stresses set up by the extruder. Bricks are dried in various ways: outdoors, in sheds, or in tunnel dryers. After drying, the bricks are fired in kilns of such type as described later in the chapter to a temperature from 875°C to somewhat above 1000°C. Combining the dryer and the kiln is a recent trend. The stiff-mud process is employed for the manufacture of practically every clay product, including all types of brick, sewer pipe, drain tile, hollow tile, fireproofing, and terra-cotta. The clay in some cases can be worked directly from a bank into the stiff-mud machine, but a more desirable product will result if the clay is ground and tempered before use. The type of clay locally available often determines the ceramic product which can be made economically. Structural-clay product fabrication has become highly mechanized; unmodernized plants cannot remain competitive.

REFRACTORIES

Refractories, termed *acid*, *basic*, and *neutral*, and also superrefractories embrace those materials used to withstand the effect of thermal, chemical, and physical effects met with in furnace procedures. Refractories are sold in the form of firebrick; silica, magnesite, chromite, and magnesite-chromite brick; silicon carbide and zirconia refractories; aluminum silicate and alumina products. The fluxes required to bind together the particles of the refractories are kept at a minimum to reduce vitrification. The possibility of shaping articles made from bodies without clay and even with no natural plasticity led to the manufacture of single-component ceramics with superior qualities, e.g., pure oxide refractories. These are monocrystalline and self-bonded as compared with the conventional vitreous-bonded refractories.

PROPERTIES OF REFRACTORIES. In making the refractory best suited for a definite operation it is necessary to consider the materials, the working temperature of the furnace where the refractory is needed, the rate of temperature change, the load applied during heats, and the chemical reactions encountered. Generally, several types of refractories are required for the construction of any one furnace, because usually no single refractory can withstand all the different conditions that prevail in the various parts of furnaces.

Chemical Properties. The usual classification of commercial refractories divides them into acid, basic, and neutral groups, although in many cases a sharp distinction cannot be made. Silica bricks are decidedly acid, and magnesite bricks are strongly basic; however, fireclay bricks are generally placed in the neutral group, though they may belong to either of these classes, depending upon the relative silica-alumina content. It is usually inadvisable to employ an acid brick in contact with an alkaline product, or vice versa. Neither chemical reactions nor physical properties are the only criteria of acceptable behavior; both should be considered. Chemical action may be due to contact with slags, fuel ashes, and furnace gases, as well as with products such as glass or steel.

Porosity. Porosity is directly related to many other physical properties of brick, including resistance to chemical attack. The higher the porosity of the brick, the more easily it is penetrated by molten fluxes and gases. For a given class of brick, those with the lowest porosity have the greatest strength, thermal conductivity, and heat capacity.

Fusion Points. Fusion points are found by the use of pyrometric cones of predetermined softening points. Most commercial refractories soften gradually over a wide range and do not have sharp melting points because they are composed of several different minerals, both amorphous and crystalline. The fusing points of these pyrometric cones are available in the literature.[11] Typical fusion points of refractories, both for pure substances and for technical products, are given in Table 6.3.

Spalling. A fracturing, or a flaking off, of a refractory brick, or block, due to uneven heat stresses or compression caused by heat is known as *spalling*.[12] Refractories usually expand when heated. Bricks that undergo the greatest expansion at the least uniform rate are the most susceptible to spalling when subjected to rapid heating and cooling.

Strength. Cold strength usually has only a slight bearing on strength at high temperatures. Resistance to abrasion or erosion is also important for many furnace constructions, such as by-product coke-oven walls and linings of the discharge end of rotary cement kilns.

Resistance to Temperature Changes. Bricks with the lowest thermal expansion and coarsest texture are the most resistant to rapid thermal changes; also, less strain develops. Bricks that have been used for a long time are often melted to glassy slags on the outside surface or even more or less corroded away.

[11]ASTM Designation C 24–79. Many other specifications for refractories and refractory materials are given in the ASTM standards.

[12]Norton, *Refractories*, 4th ed., McGraw-Hill, New York, 1968. Chap. 16, is devoted entirely to spalling and has many literature references.

Table 6.3 Fusion Temperatures of Refractories

Material	Temperature, °C
Fire-clay brick	1600–1750
Kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)	1785
Silica brick	1700
Silica (SiO_2)	1710
Bauxite brick	1732–1850
High-alumina clay brick	1802–1880
Mullite ($3Al_2O_3 \cdot 2SiO_2$)	1810
Sillimanite (Al_2SiO_5)	1816
Forsterite ($2MgO \cdot SiO_2$)	1890
Chromite ($FeO \cdot Cr_2O_3$)	1770
Chrome brick	1950–2200
Alumina (Al_2O_3)	2050
Spinel ($MgO \cdot Al_2O_3$)	2135
Silicon carbide (SiC)	2700
Magnesite brick	2200
Zirconia brick	2200–2700
Boron nitride*	2720

Chem. Eng. 70 (22) 110 (1963).

SOURCE: Norton, *Refractories*, 4th ed., McGraw-Hill, New York, 1964. For other data on refractory materials, see Perry, pp. 23–73; Chem. Eng. 70 (22) 110 (1963).

Thermal Conductivity. The densest and least porous bricks have the highest thermal conductivity. Though heat conductivity is wanted in some furnace constructions, as in muffle walls, it is not so desirable as some other properties of refractories, such as resistance to firing conditions. Insulation is desired in special refractories.

Heat Capacity. Furnace heat capacity depends upon the thermal conductivity, the specific heat, and the specific gravity of the refractory. The low quantity of heat absorbed by lightweight brick works as an advantage when furnaces are operated intermittently, because the working temperature of the furnace can be obtained in less time with less fuel. Conversely, dense, heavy fire-clay brick is best for regenerator checkerwork, as in coke ovens, glass furnaces, and stoves for blast furnaces.

MANUFACTURE OF REFRACTORIES.[13] The following physical operations and chemical conversions are used in the manufacture of refractories: grinding and screening, mixing, pressing or molding and re-pressing, drying, and burning or vitrification. Usually, the most important single property to produce in manufacture is high bulk density, which affects many of the other important properties, such as strength, volume stability, slag and spalling resistance, as well as heat capacity. For insulating refractories, a porous structure is required, which means low density.

Grinding. Obviously, one of the most important factors is the size of the particles in the batch. It is known that a mixture in which the proportion of coarse and fine particles is about 55:45, with only few intermediate particles, gives the densest mixtures. Careful screening, separation, and recycling are necessary for close control. This works very well on highly crystalline materials but is difficult to obtain in mixes of high plasticity.

Mixing. The real function of mixing is the distribution of the plastic material so as to coat thoroughly the nonplastic constituents. This serves the purpose of providing a lubricant during the molding operation and permits the bonding of the mass with a minimum number of voids.

Molding. The great demand for refractory bricks of greater density, strength, volume, and uniformity has resulted in the adoption of the dry-press method of molding with mechanically operated presses (Fig. 6.5*a*). The dry-press method is particularly suited for batches that consist primarily of nonplastic materials. In order to use high-pressure forming, it is necessary to de-air the bricks during pressing to avoid laminations and cracking when the pressure is released. When pressure is applied, the gas is absorbed by the clay or condensed. Vacuum is applied through vents in the mold box. Large special shapes are not easily adapted to machine molding.

Drying. Drying is used to remove the moisture added before molding to develop plasticity. The elimination of water leaves voids and causes high shrinkage and internal strains. In some cases drying is omitted entirely, and the small amount necessary is accomplished during the heating stage of the firing cycle.

Burning. Burning may be carried out in typical round, downdraft kilns or continuous-tunnel kilns. Two important things take place during burning: the development of a perma-

[13]Shultz and Schroth, Refractories in the 1970's—Review and Outlook for the 1980's, *Am. Ceram. Soc. Bull.* 60 (7) 691 (1981).

nent bond by partial vitrification of the mix, and the development of stable mineral forms for future service, as shown in the phase diagram Fig. 6.2. The changes that take place are removal of the water of hydration, followed by calcination of carbonates and oxidation of ferrous iron. During these changes the volume may shrink as much as 30 percent, and severe strains are set up in the refractory. This shrinkage may be eliminated by prestabilization of the materials used.

VARIETIES OF REFRACTORIES. About 95 percent of the refractories manufactured are nonbasic, with silica (acid) and fire-clay (neutral) brick predominant. Although a refractory is usually thought of in terms of its ability to withstand temperature, it is really only in exceptional cases that heat is the sole agent that affects the final destruction. It is usually caused by chemical action at the operating temperature.

Fire-Clay Brick. Fire clays are the most widely used of all available refractory materials, since they are well suited for a variety of applications. Fire clays range in chemical composition from those with a large excess of free silica to those with a high alumina content. The steel industries are the largest consumers of refractories for the linings of blast furnaces, stoves, open hearths, and other furnaces. Other industries having use for them are foundries, lime kilns, pottery kilns, cupolas, brass and copper furnaces, continuous ceramic and metallurgical kilns, boilers, gas-generating sets, and glass furnaces.

Silica Brick. Silica brick contains approximately 95 to 96% SiO_2 and about 2% lime added during grinding to furnish the bond. Silica bricks undergo permanent expansion, which occurs during firing and is caused by an allotropic transformation that takes place in the crystalline silica. When reheated, silica bricks again expand about 1.5 percent but the effect is reversible and the bricks return to size when cooled. Silica bricks are manufactured in many standard sizes by power pressing. They have a very homogeneous texture, are free from air pockets and molding defects, and possess low porosity. These are highly desirable properties for resistance to slag penetration. The physical strength of silica bricks when heated is much higher than that of those made from clay. Consequently, they are suitable for arches in large furnaces. Furnaces using these must, however, be heated and cooled gradually, to lessen spalling and cracking. Open-hearth furnaces have silica bricks in their main arch, side walls, port arches, and bulkheads, but the newest installations have superduty silica bricks and basic bricks. Superduty silica bricks have higher refractoriness and lower permeability to gases than conventional silica bricks. Because of their high thermal conductivity, silica bricks have been utilized in by-product coke ovens and gas retorts.

High-Alumina Refractories. High-alumina refractories are used increasingly to meet the demand for materials that can withstand severe conditions for which the older fire-clay and silica bricks are not suitable. High-alumina bricks are made from clays rich in bauxite and diaspore. The refractoriness and temperature of incipient vitrification increase with the alumina content (see the phase diagram in Fig. 9.2). Another valuable property of high-alumina bricks is that they are practically inert to carbon monoxide and are not disintegrated by natural-gas atmospheres up to 1000°C. Bricks with a high percentage of alumina are classed among the superrefractories, and those of almost-pure alumina (+97%) may be considered among the recently developed special refractories, termed pure oxide (see section in this chapter). High-alumina bricks are employed in the cement industry, in paper-mill refractories, and in modern boiler settings. They are also used in the lining of glass furnaces, oil-fired furnaces, and high-pressure oil stills, in the roofs of lead-softening furnaces, and in

Basic Refractories. The important basic bricks are made from magnesia, chromite, and forsterite. To achieve the required strength and other physical properties, basic bricks are usually power-pressed and are either chemically bonded or hard-burned. The disadvantages of lack of bond and volume stability in unburned basic or other bricks have been overcome by three improvements in manufacturing: (1) interfitting of grains has been developed to a maximum by using only selected particle sizes combined in the proper proportions to fill all the voids; (2) forming pressure has been increased to 70 MPa and de-airing equipment used to reduce air voids between the grains; and (3) use of a refractory chemical bond.

Magnesia Refractories. Magnesia refractories are made from domestic magnesites, or magnesia extracted from brines (Chap. 7). Magnesia bricks do not stand much load at elevated temperatures, but this difficulty has been overcome by blending with chrome ores. Many blends are possible, ranging from predominantly magnesia to predominantly chrome. In the nomenclature the predominant blend constituent is given first. There is a large price variation because of the composition variation; these bricks are among the most expensive. Chemically bonded magnesite-chrome bricks are frequently supported with mild steel to hold the brickwork and minimize spalling loss. These refractories are used in open-hearth and electric-furnace walls, in the burning zones of cement kilns, and in the roofs of various nonferrous reverberatory furnaces. Hard-burned chrome-magnesite bricks have many important physical properties because of their special composition, particle sizes, high forming pressure, and high firing temperature. They are of particular interest in basic open-hearth furnaces. A recent development is the formulation of magnesia-carbon brick for use in electric-furnace liners. It was originally developed overseas, but U.S. brickmakers have produced products containing a variety of carbon levels for various applications.

Forsterite ($2MgO \cdot SiO_2$) is employed both as a bond and as a base for high-temperature refractories. Where forsterite forms the base, refractories are generally made from alumina. In the manufacture of forsterite refractories, dead-burned magnesite is usually added to convert some accessory minerals to forsterite, which is the most stable silicate at high temperatures. For example, enstatite or clinoenstatite, occurring in the rock olivine, as mined, is converted to forsterite:

$$\underset{\text{Enstatite}}{MgO \cdot SiO_2} + \underset{\text{Magnesia}}{MgO} \rightarrow \underset{\text{Forsterite}}{2MgO \cdot SiO_2}$$

Such superrefractories have the advantages of a high melting point, no transformation during heating, and unsurpassed volume stability at high temperatures. No calcining is necessary in their preparation. The most important use of forsterite is in glass-tank superstructures and checkers, since its high chemical resistance to the fluxes employed and good strength at high temperatures allow enhanced tank output. These refractories also find many other industrial applications, e.g., in open-hearth end walls and copper-refining furnaces.

Insulating Brick. Insulating brick is of two types: for backing refractory bricks and for use in place of regular refractory bricks. Most bricks used for backing are made from naturally porous diatomaceous earth, and those of the second type, usually called lightweight refractories, are similar in composition to heavy bricks and owe their insulating value to the method of manufacture. For instance, waste cork is ground and sized, then it is mixed with fire clay, molded, and burned. In the kiln the cork burns out, leaving a highly porous, light brick. These lightweight refractories may be used safely for temperatures of 1350 to 1600°C, whereas diatomaceous-earth brick are not suitable above 1100°C under ordinary conditions.

Silicon Carbide. Superrefractories are noted for their chemical resistance and ability to withstand sudden temperature changes. In their manufacture the crude material from the silicon carbide furnace (Chap. 12) is ground, and less than 10% ceramic bond is added. The latter may be clay or finely divided silicon carbide itself. These bricks are extremely refractory and possess high thermal conductivity, low expansion, and high resistance to abrasion and spalling. They are strong mechanically and withstand loads in furnaces to temperatures up to 1400°C. Such refractories are used chiefly in muffles because of their thermal conductivity. Their ability to absorb and release heat rapidly and their resistance to spalling under repeated temperature changes make them desirable for recuperators. They are replacing carbon and aluminosilicate products in iron-making blast furnaces because of their stability under reducing conditions and good alkali resistance, in addition to their excellent thermal transfer properties.[14] Other uses are for rocket nozzles, furnace and radiant heater tubes, and combustion chambers for ceramic-based gas turbine engines.

Refractories from Crystalline Alumina or Aluminum Silicates. Research has revealed that mullite and corundum have high slag resistance and remain in the crystalline state at temperatures of 1600°C and higher (see Fig. 6.2 for a phase diagram). High-temperature kilns now furnish alumina bricks that closely approach pure corundum in properties and mullite bricks made from calcined Indian kyanite, with the old clay bond replaced by a mullite bond consisting of interlocking crystals. Such refractories are used where severe slagging occurs.

Electrocast or Corhart Refractories. Many kinds of bonded refractories are made from electrically fused mullite. They are manufactured by introducing a mixture of diaspore clays of high alumina (to furnish a $3Al_2O_3/2SiO_2$ ratio) content into the top of an electric furnace. If necessary, these are adjusted to furnish the stable mullite ratio of $3Al_2O/2SiO_2$. Molten aluminum silicate at 1800°C is tapped from the furnace at intervals and run into molds built from sand slabs. The molds containing these blocks are annealed from 6 to 10 days before the blocks are usable. The refractory obtained from this process has a vitreous, nonporous body that shows a linear coefficient of expansion of about one-half that of good firebrick. The blocks cannot be cut or shaped, but may be ground on Alundum wheels; however, skill in casting has progressed rapidly, and now many sizes and intricate shapes are available. This electrocast has only 0.5 percent voids, in contrast to the usual 17 to 29 percent of fire-clay blocks. Cast refractories are employed in glass furnaces, in linings of hot zones of rotary kilns, in modern boiler furnaces exposed to severe duty, and in metallurgical equipment such as forging furnaces. These refractories have the advantages of long life and minimum wear, against which must be balanced their greater initial cost. A newer and superior variety of fused cast refractories, with from 83 to 95% alumina, is available. Here the interstitial glass content is greatly reduced, along with voids induced during the usual casting process.

Pure Oxide Refractories. The refractories industry is constantly faced with increased demands for products which will withstand higher temperatures and more severe operating conditions. To meet these requirements, a group of special pure oxide refractories has been developed. Their superior qualities are based mostly on freedom from fluxes. Refractory oxides of interest in order of increasing cost per unit volume include alumina, magnesia,

[14]Cole, Refel: A "Hot" Material in High-Temperature Ceramics, *Ceram. Ind.* 116 (3) 38 (1981).

zirconia, beryllia, and thoria. All have been developed commercially for light refractory products. The first three have certain properties in common: (1) they are of high purity (a minimum of 97% alumina, magnesia, or stabilized zirconia), and (2) they are principally composed of electrically fused grains. Beryllia is not used commercially for heavy wear because of its high cost and volatilization above 1650°C in the presence of water vapor. Thoria has a number of disadvantages, particularly since its radioactivity places it under the control of the Atomic Energy Commission.

Of these pure oxide[15] refractories the material that has the widest application is *sinter alumina*. It is used successfully at temperatures up to about 1870°C. *Magnesia* is a basic refractory and is easily reduced at high temperatures. Its applications are limited to oxidizing atmospheres at temperatures not much over 2200°C. Since pure *zirconia* undergoes a *crystalline change from monoclinic to tetragonal* form at about 980°C, accompanied by a drastic volume change on inversion, stabilization of the crystal structure to the cubic form, which undergoes no inversion, is necessary. This is accomplished by adding certain metallic oxides (particularly CaO and MgO). Processing temperatures in the range of 2550 to 2600°C are now commercial with available fused, stabilized zirconia. The only present large-scale use is as kiln furniture in the firing of barium titanate resistors, but future substantial usage seems probable.

SPECIALIZED CERAMIC PRODUCTS[16]

CERAMIC COMPOSITES. Structures of metallic honeycombs or webbings, impregnated with a ceramic phase, derive strength from high-alloy metals and good thermal properties from ceramic foams. The temperature limits of such bonded materials are exceedingly high; they are employed for aerospace hardware such as heat shields, rocket nozzles, and ram-jet chambers. *Cermets* comprise one of a group of composite materials consisting of an intimate mixture of ceramic and metallic components, usually in the form of powder. These are compacted and sintered in order to obtain certain physical properties not found solely in either of the components; for example, they are used in linings for brakes and clutches because of the greater weights and higher speeds involved and also nonlubricating bearings in the temperature range from 370 to 815°C.

Reaction bonded ceramic-metal composites are formed by a chemical reaction that bonds the two materials when heated below the melting point of either. The ceramic acts as a catalyst to cause corrosion of the metal to a metal oxide. As the metal oxide is formed crystals

[15]Alumina is a versatile chemical and is used in its various forms and purities as follows: (1) as raw material for metallic aluminum; (2) as "impure fused alumina" when bauxite is fused; (3) as "pure fused alumina" when pure dried alumina is fused; (4) as single-crystal Al_2O_3, or sapphire (Chap. 15); (5) as sinter alumina when grains are united by incipient surface melting or sintering.

[16]Lachman, Bagley, and Lewis, Thermal Expansion of Extruded Cordierite Ceramics, *Amer. Ceramic Soc. Bull.* 60 (2) 202 (1981); Leiser, Smith, and Goldsmith, Developments in Fibrous Refractory Composite Insulation, *Amer. Ceram. Soc. Bull.* 610 (11) 1201 (1981); Allen and Smith, Energy Savings in Furnaces Using Ceramic Fiber Modules, *Ceramic Engineering and Science Proceedings*, p. 232, March–April 1981. Reactions Bonding Is Ready to Go to Work, *Chem. Week* 132 (7) 21 (1983).

of the oxide grow into the crystal structure of the ceramic. The bond is extremely strong and permanent and forms quickly, although for optimum strength the two materials are usually kept hot for several hours while clamped together. This bonding can occur between all metals and most ceramics, but the strongest bonds are formed between the noble metals (such as platinum, gold, and silver) and oxide ceramics of alumina, magnesia, silica, zirconia, and beryllia. Several applications for these materials are suggested such as gold-coated ceramic wafers for semiconductor chips, zirconia-lined steel for corrosion-resistant uses, and for producing ceramic-capped gold dental crowns. The process also works well with gemstones, permitting a permanent bond between the gold setting and the gemstone.

Various materials can be blown or drawn into fibers which are especially useful for high-temperature insulation. A composite of blown microquartz fiber (1 to 3 μm diameter) and 0.31 cm lengths of drawn alumino-borosilicate fiber (1 to 11 μm diameter) which requires no bonding agent has been produced. The use of blankets or modules of ceramic fibers for heat-treating insulation for porcelain enameling furnaces and ceramic kiln boilers has given fuel savings of up to 30 percent.

FERROELECTRIC AND FERROMAGNETIC CERAMICS. The most common ceramic type in this class is barium titanate ($BaTiO_3$). Titania and its compounds exhibit unusual properties useful in electrical applications, the most important of which involves high capacity at various frequencies. The shortage of mica during World War II gave impetus to the development of synthetic capacitators. Procedures used in fabricating titania and titanate bodies are ceramic in character. Ferromagnetic ceramic materials have been responsible for important advances in the design of electronic equipment; they are used in television sets, computers, magnetic switches, wideband transformers, recorders, and memory devices.

HIGH-ALUMINA CERAMICS. These are mechanically strong, dense materials, unlike refractories which are usually porous. Most high-alumina ceramics are used to take advantage of their wear resistance, corrosion resistance, and dimensional stability rather than their ability to resist high temperatures. High alumina denotes 85% or more by weight of Al_2O_3. Uses include linings for mining chutes and slides, insulators for electrostatic precipitators, respirator valves, and precision machine components.

VITREOUS ENAMEL[17]

Porcelain or vitreous enamel is a ceramic mixture containing a large proportion of fluxes applied cold and fused to the metal at moderate red heat. Complete vitrification takes place. The application of enamel to gold, silver, and copper is one that dates back to the ancients. Long valued as a material of great beauty in the field of decorative art, it has come into general commercial use because it provides a product of great durability and wide application, it is easy to clean and resists corrosion. Current uses are in plumbing fixtures, cooking utensils, industrial equipment, and glass-enameled steel for chemical use. The household appliances market has been diminished by the modern use of baked-on organic coatings, but

[17] Rogers, The Future of Porcelain Enameling, *Ceram. Ind.* 116 (2): 49, 1981; Faust, Evele, and Smith, Analysis of Two Coat/One Fire Powder Adherence, *Ceram. Eng. Sci. Proc.* p. 256, March–April 1981.

new markets have developed in electroluminescent lighting and in the automobile industry. In the latter there is a multimillion-dollar market for frits in manufacturing tailpipes and mufflers; about 0.5 kg of frit is used for each muffler and 0.4 kg for each tailpipe.

RAW MATERIALS. These must not only have high purity but also fineness, suitable mineral composition, proper grain shape, and other physical characteristics, depending on the specific enamel. The raw materials used in the enamel industry may be divided into six different groups: refractories, fluxes, opacifiers, colors, floating agents, and electrolytes. *Refractories* include such material as quartz, feldspar, and clay, which contribute to the acidic part of the melt and give body to the glass. *Fluxes* include such products as borax, soda ash, cryolite, and fluorspar, which are basic in character and react with the acidic refractories to form the glass. They tend to lower the fusion temperature of enamels. *Opacifiers* are compounds added to the glass to give it the white opaque appearance so characteristic of vitreous enamels. They are of two principal types: insoluble opacifiers (titanium dioxide, tin oxide, and zirconium oxide) and devitrification opacifiers (cryolite and fluorspar). In 1945 titanium dioxide–opacified enamels were commercially developed, and they have gained general acceptance in the industry because of high opacity and good acid resistance. Their chief advantage is that they may be applied more thinly than the best previous opacifiers and therefore are more resistant to chipping, as well as being smoother and of greater reflectance. Devitrification opacifiers also act as fluxes, rendering the enamel more fusible. *Color* materials may be oxides, elements, salts, or frits, and may act either as refractories or as fluxes. *Floating agents* such as clay and gums are chosen to suspend the enamel in water. A pure plastic clay is required. To peptize the clay and properly suspend the enamel, *electrolytes* are added, such as borax, soda ash, magnesium sulfate, and magnesium carbonate.

MANUFACTURE OF THE FRIT. The preparation of the enamel glass, or frit, is similar to the first stages of the manufacture of ordinary glass. The raw materials are mixed in the proper proportions and charged into a melting furnace maintained near 1370°C, from 1 to 3 h. After the batch has been uniformly melted, it is allowed to pour from the furnace into a quenching tank of cold water, shattering the melt into millions of friable pieces. This material is called *frit*. Enamel is normally made in a wet process by grinding the ingredients, principally a mixture of frit and clay, the latter as a suspension aid, in a ball mill, and then passing through a 200-mesh screen.

A major step in process simplification has been the development of electrostatic-powder spray application. The powder is supplied ready to use, eliminating the need for in-plant milling. This technology also saves the energy used to remove the water in the conventional wet processing.

PREPARATION OF METAL PARTS. The success of enameling depends on the nature and uniformity of the metal base to which the enamel is fused and on obtaining a parallelism between the coefficients of expansion of the enamel and the metal. In the cast-iron enameling industry castings are frequently made in the same factory in which they are enameled. The sheet-metal enameler usually purchases sheets to meet a definite specification. Before the liquid enamel (suspension in water) is applied to the metal, the surface must be thoroughly cleaned of all foreign matter, so that the enamel coating will adhere well to the metal and also not be affected itself. Sheet metal is cleaned by pickling in dilute hydrochloric or sulfuric acid at 60°C after the iron has been annealed.

The advent of the powder application has brought with it the pickle-free metal preparation. Only cleaning of the base metal is necessary for the satisfactory coating with powder.

Efforts are also being made to perfect a no-pickle wet process.[18] The disposal of pickle waste has become very costly because of modern environmental concerns and regulations. The development of no-pickle processes for metal preparation will benefit both the producer and the public.

APPLICATION OF THE ENAMEL. Sheet-iron coats are generally applied by dipping or slushing since the ware is usually coated on all sides. Slushing differs from dipping in that the enamel slip is thicker and must be shaken from the ware. A third method of application is spraying. Cast-iron treatment is very similar to that for sheet iron. The enamel is air-dried, and colors are brushed and stenciled on. The enamel is usually applied in two coats for premium ware.

In the powder process the steel is coated by electrostatic spraying. This process is evolving to a two-coat, one-fire system consisting of a thin powder base coat and a powder cover coat. Both coats are cured at once in a single fire. This produces a quality product at a much lower cost than the conventional process.

FIRING. All enamels must be fired on the ware to melt them into a smooth, continuous, glassy layer. The requirements for successful firing of a good enamel are: (1) proper firing temperature, 750 to 800°C, (2) time, 1 to 15 min, (3) proper support of the ware, (4) uniform heating and cooling of the ware, and (5) an atmosphere free from dust. Today enamel coats average about 0.165 mm as compared with 0.66 mm a few years ago. Increasing numbers of products are being fabricated with a single coat, less subject to chipping, because of the use of better opacifiers. The special enamel- or glass-lined equipment so extensively used in chemical plants is tested by high-frequency electrical testers to exclude defects that only this method will detect, but that in the course of use would offer an avenue for corrosive penetration.

KILNS[19]

The vitrification of ceramic products and the prior chemical conversions dehydration, oxidation, and calcination are carried out in kilns that may be operated in a periodic or continuous manner. All the newer installations are continuous-tunnel kilns, which have many advantages over batch kilns, such as lower labor costs, greater fuel efficiency, shorter processing-time cycle, and better operating control. Gas, coal, and oil are the most economical fuels, hence are more commonly used for firing; electricity is used in some instances.

CONTINUOUS KILNS. The most important kilns are the continuous car *tunnel kilns* used for the firing of brick, tile, porcelain, tableware, and refractories. There are two general types of such kilns: the direct-fired type, where combustion gases burn directly among the wares, and the indirect (muffle) type, where the products of combustion are not allowed to contact the wares. The wares are loaded directly onto open cars or enclosed in saggers which keep them clean. The cars pass through the tunnel counterflow to the combustion gases from the high-fire zone. The wares may be loaded on rolls in a *roller hearth kiln* instead of into cars that

[18]Carter and Sinkovic, No-Pickle Wet Process Passes Experimental Tests, *Ceram. Ind.* **117** (3) 41 (1981); Wright, A Look Ahead, The P. E. Plant of 1990, *Ceram. Ind.* **116** (6) 42 (1981).

[19]Norton, op. cit., pp. 206, 210, 218, tabulates fuel consumption for kilns.

move through the kiln. The conveyor system consists of a continuous belt of silicon carbide rolls. This type of kiln is particularly suited for the production of electronic parts that must meet exacting specifications. The continuous *chamber kiln* consists of a series of connected chambers. The heat from one chamber is passed to another countercurrent to the wares. Because the chambers are burned in succession, the operation is continuous. There is always one chamber cooling, another being fired, and another being heated by the waste heat of the two other chambers. This type of kiln is used to burn brick and tile.

PERIODIC KILNS. These are not as fuel efficient as continuous kilns but are more versatile.

Downdraft kilns, which are round or rectangular in shape, are used in burning face brick, sewer pipe, stoneware, tile, and common brick. In them the heat is raised from room temperature to the finishing temperature for each burning operation. The kiln is "set" (filled with wares to be burned), the heating is started, and the temperature is raised at a definite rate until the firing temperature is reached. The downdraft kiln is so named because the products of combustion go down in passing over the wares set in the kiln. The *updraft kiln* has been most commonly used in burning potteryware but is rapidly being replaced by tunnel kilns. Common bricks are burned in *scove kilns*, which are really variations on the updraft kiln. The kiln itself is built from green brick, and the outside walls are daubed, or "scoved," with clay.

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Chapter 7

Portland Cements, Calcium, and Compounds Magnesium

The industrial uses of limestone and cements have provided important undertakings for chemists and engineers since the early years when lime mortars and natural cements were introduced. In modern times one need only mention reinforced-concrete walls and girders, tunnels, dams, and roads to realize the dependence of present-day civilization upon these products. The convenience, cheapness, adaptability, strength, and durability of cement products have been a foundation of these applications.

PORTLAND CEMENTS

In spite of the modern concrete roads and buildings everywhere around us, it is difficult to realize the tremendous growth of the cement industry during the past century. Humans had early discovered certain natural rocks which, through simple calcination, gave a product that hardened on the addition of water. Yet the real advance did not take place until physiochemical studies and chemical engineering laid the basis for the modern efficient plants working under closely controlled conditions with a variety of raw materials.

HISTORICAL. Cement dates back to antiquity, and one can only speculate as to its discovery.[1] A cement was used by the Egyptians in constructing the Pyramids. The Greeks and Romans used volcanic tuff mixed with lime for cement, and a number of these structures are still standing. In 1824 an Englishman, Joseph Aspdin, patented an artificial cement made by the calcination of an argillaceous limestone. He called this "portland" because concrete made from it resembled a famous building stone obtained from the Isle of Portland near England. This was the start of the portland cement industry of today. The hard clinker resulting from burning a mixture of clay and limestone or similar materials is known by the term portland cement to distinguish it from natural or pozzolan and other cements. Concrete and cement are not synonomous terms. Concrete is artificial stone made from a carefully controlled mixture of cement, water, and fine and coarse aggregate (usually sand and coarse rock).

[1]ECT, 3d ed., vol. 5, 1979, pp. 163–192 (excellent summary); Skalny and Daugherty, Everything You Always Wanted to Know About Portland Cement, *CHEMTECH* 2 (1) 38 (1972).

USES AND ECONOMICS. Before 1900 concrete was relatively little used in this country because the manufacture of portland cement was an expensive process. Thanks to the invention of labor-saving machinery, cement is now low in cost and is applied everywhere in the construction of homes, public buildings, roads, industrial plants, dams, bridges, and many other structures. Table 7.1 indicates the large volume of this industry. In 1980 there were 142 plants in the United States producing portland cement. It is interesting that the 10 largest plants produced 48 percent of the total and the 20 largest plants produced 72 percent.

TYPES OF PORTLAND CEMENTS. *Portland cement* has been defined as[2] "the product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates, usually containing one or more forms of calcium sulfate as an interground addition." Hydraulic calcium silicates possess the ability to harden without drying or by reaction with atmospheric carbon dioxide, thus differentiating them from other inorganic binders such as plaster of paris. The reactions involved in the hardening of cement are hydration and hydrolysis. Five types (Table 10.2) of portland cement are recognized in the United States.

Type I. *Regular* portland cements are the usual products for general construction. There are other types of this cement, such as white, which contains less ferric oxide, oil-well cement, quick-setting cement, and others for special uses.

Type II. *Moderate-heat-of-hardening* and *sulfate-resisting* portland cements are for use where moderate heat of hydration is required or for general concrete construction exposed to moderate sulfate action. The heat evolved from these cements should not exceed 295 and 335 J/g after 7 and 28 days, respectively.

Type III. *High-early-strength* (HES) cements are made from raw materials with a lime-to-silica ratio higher than that of Type I cement and are ground finer than Type I cements. They contain a higher proportion of tricalcium silicate (C_3S) than regular portland cements. This, with the finer grinding, causes quicker hardening and a faster evolution of heat. Roads constructed from HES cement can be put into service sooner than roads constructed from regular cement.

[2]ASTM Specification 150-81.

Table 7.1 Portland Cement Shipments by Types, 1981
(in thousands of metric tons and thousands of dollars)

	Quantity	Value	Average Value per Metric Ton
General use and moderate (Types I and II)	56,852	192,940	56.16
High-early-strength (Type III)	2,333	135,214	57.94
Sulfate-resisting (Type V)	182	12,633	69.49
Oil well	2,974	203,990	68.58
White	302	42,721	141.56
Portland slag and pozzolan	621	38,189	61.51
Expansive	50	3,648	72.97
Miscellaneous*	524	36,376	69.47
Total or average	63,838	665,711	57.43

*Includes waterproof cement and low-heat (Type IV).

SOURCE: *Minerals Yearbook 1981*, vol. 1, Dept. of the Interior, 1982, p. 194.

***Table* 7.2** Chemical Specifications for Portland Cements

Constituent	Regular, Type I	Moderate-Heat-of-Hardening Type II	High-Early-Strength, Type III	Low-Heat-of-Hydration, Type IV	Sulfate-Resisting, Type V
Sliicon dioxide (SiO_2), min %	—	20.0			
Aluminum oxide (Al_2O_3), max %	—	6.0	—	—	*
Ferric oxide (Fe_2O_3), max %	—	6.0	—	6.5	*
Magnesium oxide (MgO), max %	5.0	6.0	6.0	6.0	6.0
Sulfur trioxide (SO_3), max. %					
When $3CaO \cdot Al_2O_3$ is 8% or less	2.5	3.0	3.5	2.3	2.3
When $3CaO \cdot Al_2O_3$ is more than 8%	3.0	—	4.5		
Loss on ignition, max %	3.0	3.0	3.0	2.5	3.0
Insoluble residue, max %	0.75	0.75	0.75	0.75	0.75
Tricalcium silicate ($3CaO \cdot SiO_2$), max %	—	—	—	35	
Dicalcium silicate ($2CaO \cdot SiO_2$) min %	—	—	—	40	
Tricalcium aluminate ($3CaO \cdot Al_2O_3$), %	—	8	15	7	5

*The tricalcium aluminate shall not exceed 5% and the tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) plus twice the amount of tricalcium aluminate shall not exceed 20%

SOURCE: ASTM Designation C 150–80.

Type IV. *Low-heat* portland cements contain a lower percentage of C_3S and tricalcium aluminate (C_3A), thus lowering the heat evolution. Consequently, the percentage of tetracalcium aluminoferrite (C_4AF) is increased because of the addition of Fe_2O_3 to reduce the amount of C_3A (Table 7.4). Actually, the heat evolved should not exceed 250 and 295 J/g after 7 and 28 days, respectively, and is 15 to 35 percent less than the heat of hydration of regular or HES cements.

Type V. *Sulfate-resisting* portland cements are those which, by their composition or processing, resist sulfates better than the other four types. Type V is used when high sulfate resistance is required. These cements are lower in C_3A than regular cements. In consequence of this, the C_4AF content is higher.

Air Entrainment. The use of air-entraining agents (minute quantities of resinous materials, tallows, and greases) is important. These agents increase the resistance of the hardened concrete to scaling from alternate freezing and thawing and the use of de-icers (such as $CaCl_2$). Federal specifications permit the addition of an air-entraining material to each of the three types, which are then designated IA, IIA, and IIIA.

MANUFACTURING PROCEDURES. Two types of materials are necessary for the production of portland cement, one rich in calcium (calcareous), such as limestone, chalk, etc., and one

rich in silica (argillaceous) such as clay. Formerly a large amount of cement was made from argillaceous limestone, known as *cement rock*, found in New Jersey and the Lehigh district of Pennsylvania. In addition to natural materials, some plants use blast-furnace slag and precipitated calcium carbonate obtained as a by-product in the alkali and synthetic ammonium sulfate industry. Sand, waste bauxite, and iron ore are sometimes used in small amounts to adjust the composition of the mix. Gypsum (4 to 5%) is added to regulate the setting time of the cement.

These raw materials (Table 7.3) are finely ground, mixed, and heated (burned) in a rotary kiln to form cement clinker. Table 7.4 lists the predominant compounds that are formed during calcining. The cement industry uses the following abbreviations for these clinker compounds:

$CaO = C$	$MgO = M$	$CO_2 = \bar{C}$
$SiO_2 = S$	$SO_3 = \bar{S}$	$H_2O = H$
$Al_2O_3 = A$	$Na_2O = N$	
$Fe_2O_3 = F$	$K_2O = K$	

Thus Ca_3SiO_5 $(3CaO \cdot SiO_2) = C_3S$

Various reactions, such as evaporation of water, evolution of carbon dioxide, and reaction between lime and clay, take place during the burning (Table 7.5). Most of these reactions proceed in the solid phase, but, toward the end of the process, the important fusion occurs. Liquid formation begins at 1250°C and probably no appreciable formation of C_3S occurs below this temperature. C_3S is the chief strength-producing constituent of cement and during

***Table* 7.3** Raw Matrials Used in Producing Portland Cement in the United States (in thousands of metric tons)

Raw Materials	1979	1980	1981
Calcareous			
Limestone (includes aragonite, marble, chalk)	73,725	71,164	66,380
Cement rock (includes marl)	28,167	22,717	24,204
Oyster shell	3,089	3,080	2,809
Argillaceous			
Clay	6,378	5,654	5,219
Shale	3,899	3,811	3,317
Other (includes Staurolite, bauxite, aluminum dross, pumice and volcanic material)	329	284	193
Siliceous			
Sand	1,934	1,813	1,631
Sandstone and quartz	734	607	667
Ferrous			
Iron ore, pyrites, mill-scale and other iron-bearing material	966	1,068	1,040
Other			
Gypsum and anhydrite	3,931	3,508	3,272
Blast furnace slag	439	120	86
Fly ash	463	546	688
Other	5	155	147
Total	124,059	114,529	109,654

SOURCE: *Minerals Yearbook 1981*, vol. 1, Dept. of the Interior, 1982, p. 183.

Table 7.4 Clinker Compounds

Formula	Name	Abbreviation
$2CaO \cdot SiO_2$	Dicalcium silicate	C_2S
$3CaO \cdot SiO_2$	Tricalcium silicate	C_3S
$3CaO \cdot Al_2O_3$	Tricalcium aluminate	C_3A
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	Tetracalcium aluminoferrite	C_4AF
MgO	Magnesium oxide in free state	M

NOTE: See Table 10.7 for amounts in cement.

its formation the free lime present is reduced to a small amount. Between 20 and 30 percent of the reactions take place in the final fluid phase.[3]

Cement clinker is manufactured by both wet and dry processes. In both processes *closed-circuit grinding* is preferred to *open-circuit grinding* in preparing the raw materials because in the former the fines are passed on and the coarse material returned, whereas in the latter the raw material is ground continuously until its mean fineness has reached the desired value (see Fig. 10.2 for some grinding hookups). However, Perry[4] presents more details of actual grinding circuits with power requirements. The *wet process*, though the original one, is being displaced by the *dry process*, especially for new plants, because of the saving in heat, accurate control, and mixing of the raw mixture it affords. At the end of 1980, dry process plants accounted for 45 percent of the total cement production capacity,[5] but used only 40.4 percent of the industry's total energy consumption. These processes are illustrated in the generalized flowchart in Fig. 10.1. In the wet process the solid material, after dry crushing, is reduced to a fine state of division in wet tube or ball mills and passes as a slurry through bowl classifiers or screens. The slurry is pumped to correcting tanks, where rotating arms make the mixture homogeneous and allow the final adjustment in composition to be made. In some plants, this

[3]Lea, *The Chemistry of Cement and Concrete*, 3d ed., Edward Arnold, London, 1970.

[4]Perry, Cement, Lime, and Gypsum, pp. 8-50 to 8-52.

[5]*Energy Report of U.S. Portland Cement Industry*, Portland Cement Association, July, 1981.

Table 7.5 Reactions during Clinker Formation

Temperature, °C	Reaction	Heat Change
100	Evaporation of free water	Endothermic
500 and above	Evolution of combined water from clay	Endothermic
900 and above	Crystallization of amorphous dehydration products of clay	Exothermic
900 and above	Evolution of carbon dioxide from calcium carbonate	Endothermic
900–1200	Main reaction between lime and clay	Exothermic
1250–1280	Commencement of liquid formation	Endothermic
1280 and above	Further formation of liquid and completion of formation of cement compounds	Probably endothermic on balance

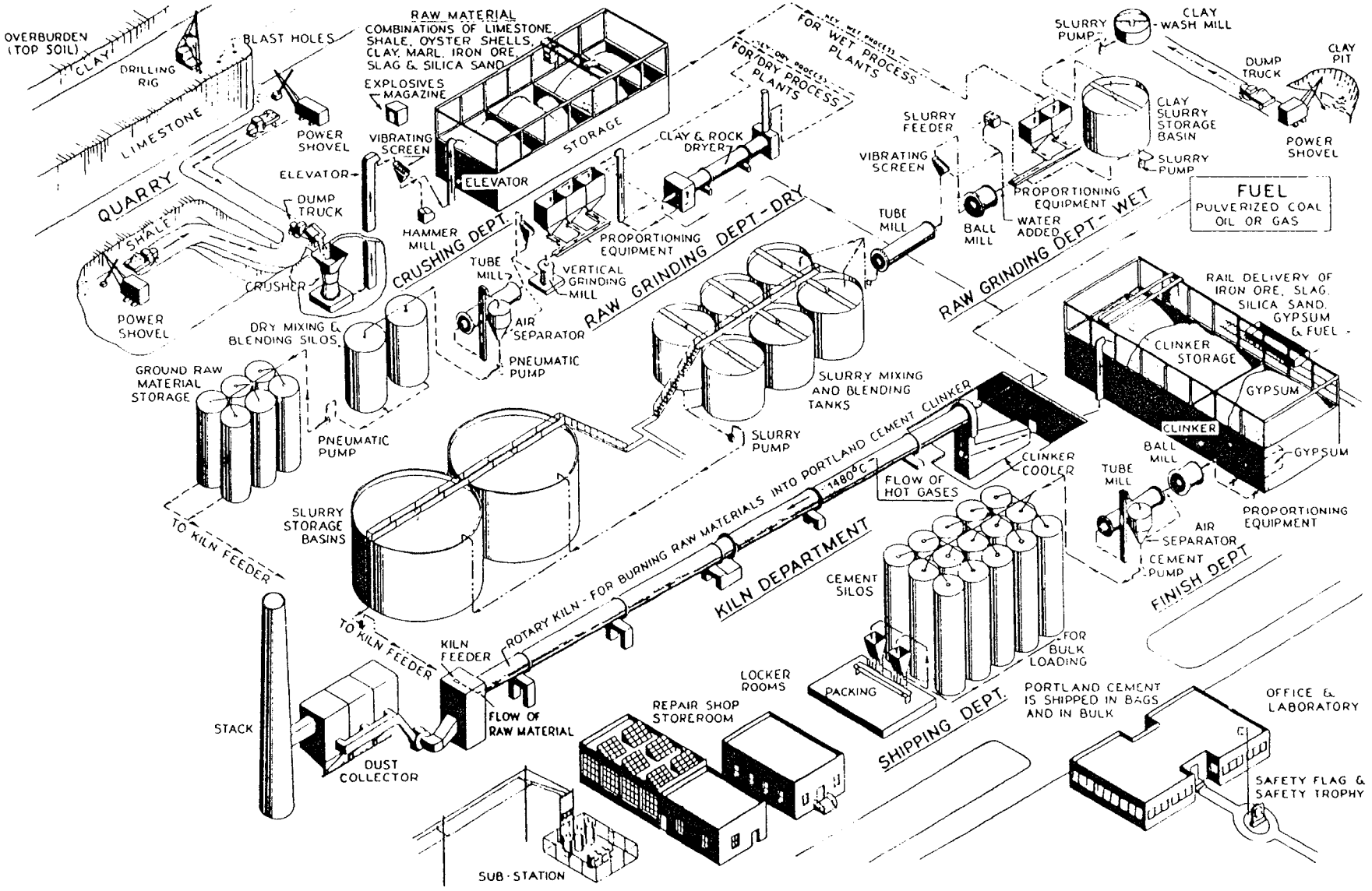

Fig. 7.1. Isometric flowchart for the manufacture of portland cement by both dry and wet processes. *(Portland Cement Assoc.)*

slurry is filtered in a continuous rotary filter and fed into the kiln. The *dry process* is especially applicable to natural cement rock and to mixtures of limestone and clay, shale, or slate. In this process the materials may be roughly crushed, passed through gyratory and hammer mills, dried, sized, and more finely ground in tube mills, followed by air separators. Proportioning equipment is included in the sequences. Before entering the kiln a thorough mixing and blending by air or otherwise takes place. This dry, powdered material is fed directly to rotary kilns, where the previously mentioned chemical reactions take place. Heat is provided by burning oil, gas, or pulverized coal, using preheated air from cooling the clinker. The tendency in recent years has been to lengthen the rotary kiln in order to increase its thermal efficiency. Dry-process kilns may be as short as 45 m, but in the wet process, 90- to 180-m kilns are not uncommon. The internal diameter is usually from 2.5 to 6 m. The kilns are rotated at from ½ to 2 rpm depending on size. The kilns are slightly inclined, so that materials fed in at the upper end travel slowly to the lower firing end, taking from 1 to 3 h. In order to obtain greater heat economy, part of the water is removed from wet process slurry. Some of the methods used employ slurry filters and Dorr thickeners. Efficient air pollution control equipment such as baghouses or electrostatic precipitators are now required for kilns.[6] Waste-heat boilers are sometimes used to conserve heat and are particularly economical for dry process cement, since the waste gases from the kiln are hotter than those from the wet process and may reach 800°C. Because the lining of the kiln has to withstand severe abrasions and chemical attack at the high temperatures in the clinkering zone, the choice of a refractory lining is difficult. For this reason high-alumina and high-magnesia bricks are widely used. Computers are now used to improve kiln control. The final product formed consists of hard, granular masses from 3 to 20 mm in size, called *clinker*. The clinker is discharged from the rotating kiln into the air-quenching coolers, which quickly bring its temperature down to approximately 100 to 200°C. These coolers simultaneously preheat the combustion air. Pulverizing, followed by fine grinding in the tube ball mills and automatic packaging, completes the process. During the fine grinding, setting retarders, such as gypsum, plaster, or calcium lignosulfonate, and air-entraining, dispersing, and waterproofing agents are added. The clinker is ground dry by various hookups, as illustrated in Fig. 7.2 and by Perry.

The entire cement process can be monitored by x-ray machines connected with programmable calculators in order to constantly sample the product and then automatically adjust the raw mill feed to produce the desired product.[7] The cement industry is the nation's sixth largest industrial user of energy. In 1980 the production of 61.75×10^6 t of clinker consumed 11×10^6 t of coal, 500×10^3 m^3 oil, and 1.78×10^6 m^3 natural gas.[7a] For this reason, much effort has been expended in devising more energy efficient technology. One proposal suggests the use of fluoride-containing fluxes to reduce the temperature necessary for clinker formation.[8]

COMPOUNDS IN CEMENTS. Portland cements contain a mixture of compounds (previously listed) present in amounts partly dependent on the degree of attainment of equilibrium conditions during burning. Tables 7.6 and 7.7 give analyses of various types of portland cement and some typical compositions of regular cements. From these analyses it is seen that portland cement composition approaches a rough approximation to the system CaO–SiO_2 and succes-

[6]Cements' Changing Scene, *Chem. Eng.* 81 (13) 103 (1974); Voldbaek and Cooke, *Rock Prod.* 83 (4) 108 (1980).

[7]Kruegel, X-Ray Control of Cement Process, *Rock Prod.* 81 (4) 132 (1979).

[7a]t = 1000 kg.

[8]... Process in Cement Manufacture, *Rock Prod.* 83 (4) 52 (1980).

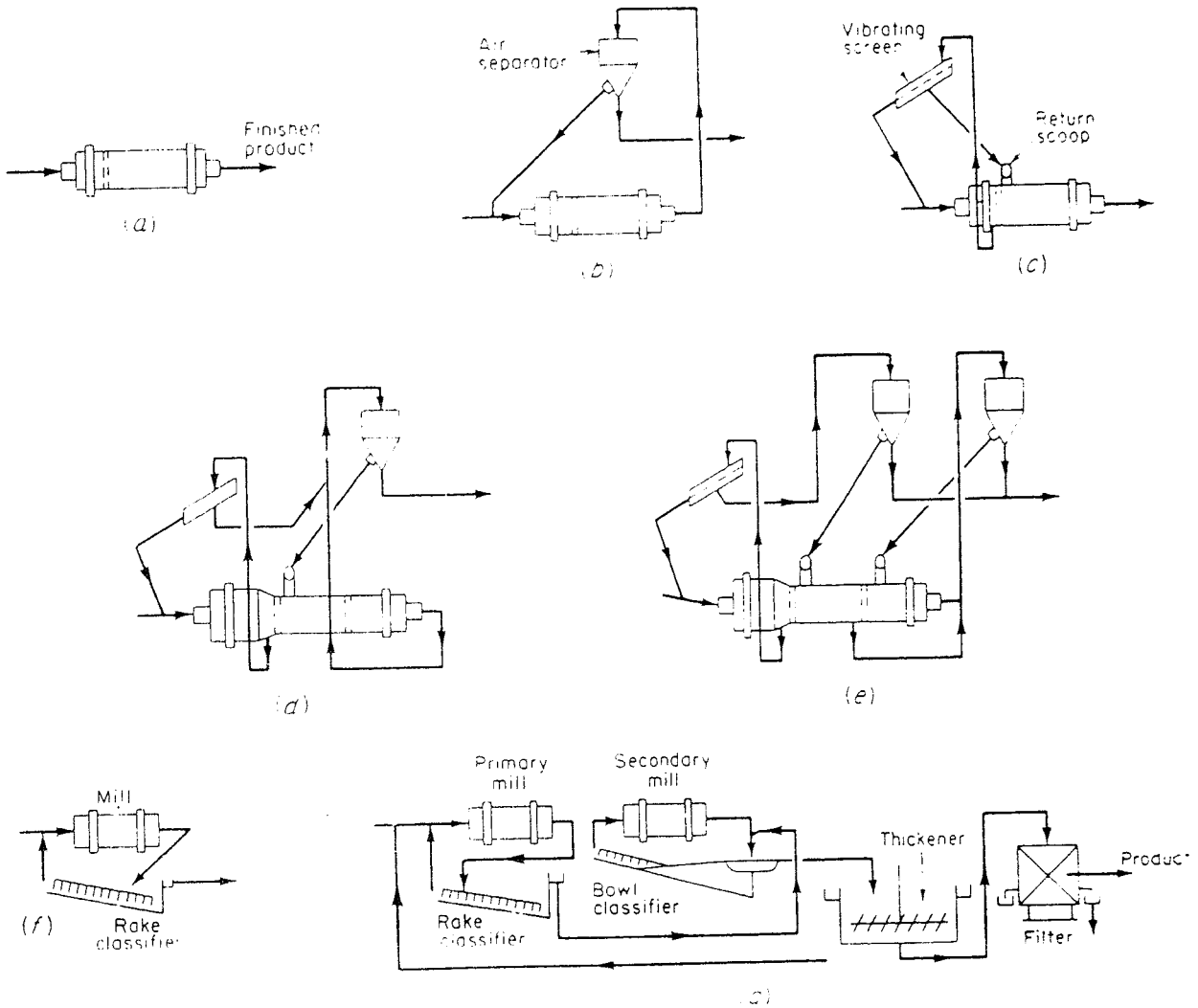

Fig. 7.2. Dry- and wet-grinding hookups. (*a*) Simple two-compartment mill in open circuit; (*b*) two-compartment mill closed-circuited with air separator; (*c*) two-stage setup with primary compartment closed-circuited; (*d*) efficient two- or three-compartment circuit closed with a screen and air separator; (*e*) highly efficient three-stage system closed-circuited in each stage; (*f*) single-stage mill closed-circuited with rake classifier; (*g*) modern double-stage circuit employing four different types of separating equipment. (*Source*: CPI.)

***Table* 7.6** Analyses of Portland Cements (in percentage)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Alkali Oxides	SO_3
			Regular Cement (Average of 102)				
Minimum	61.17	18.58	3.86	1.56	0.60	0.66	1.32
Maximum	66.92	23.26	7.44	6.18	5.24	2.9	2.26
Average	63.85	21.08	5.79	2.86	2.47	1.4	1.73
			High-Early-Strength (Average of 8; High C_3S)				
Minimum	62.7	18.0	4.1	1.7	—	—	2.2
Maximum	67.5	22.9	7.5	4.2	—	—	2.7
Average	64.6	19.9	6.0	2.6	—	—	2.3
			Low-Heat-of-Hardening (Average of 5; Lower C_3S and C_3A, Higher C_2S and C_4AF				
Minimum	59.3	21.9	3.3	1.9	—	—	1.5
Maximum	61.5	26.4	5.4	5.7	—	—	1.9
Average	60.2	23.8	4.9	4.9	—	—	1.7

***Table* 7.7** Potential Compound Composition of Some Typical Cements (in percentage)

	C_3S	C_2S	C_3A	C_4AF
Type I	55	19	10	7
Type II	51	24	6	11
Type III	56	19	10	7
Type IV	28	49	4	12
Type V	38	43	4	9

SOURCE: ECT, 3d ed., vol. 5, 1979, p. 171.

sively closer approximations to the systems $CaO–SiO_2–Al_2O_3$, $CaO–SiO_2–Al_2O_3–Fe_2O_3$, and $CaO–SiO_2–Al_2O_3–Fe_2O_3–MgO$. A complete understanding of portland cement would require knowledge of the phase-equilibrium relations of the high-lime portions of all the two-, three-, four-, and five-component systems involved. Of these, all 12 of the principal two- and three-component systems, and the parts of the four-component systems, $CaO–SiO_2–Al_2O_3–Fe_2O_3$ and $CaO–SiO_2–Al_2O_3–MgO$, in which portland cement compositions are located, are known. In 1946 part of the five-component system, $CaO–MgO–Al_2O_3–Fe_2O_3–SiO_2$, was studied by Swayze;[9] such studies are being continued. Modern cement technology owes much to Rankin and Wright[10] of the Geophysical Laboratory.

SETTING AND HARDENING OF CEMENT. Although many theories have been proposed to explain the setting and hardening of cement, it is generally agreed that *hydration* and *hydrolysis*[11] are involved. The hydration products have very low solubility in water. If this were not true, concrete in contact with water would be rapidly attacked. Much attention has been given to the heat evolved during the hydration of cement. The various compounds contribute to the heat of hardening (basis, equal weights, i.e., gram for gram) after 28 days, as follows:[12]

$$C_3A > C_3S > C_4AF > C_2S$$

Table 10.8 shows why low-heat-of-hardening cements are made low in C_3A and C_3S but high in C_2S. This is accomplished (1) by adding more Fe_2O_3, which takes the Al_2O_3 out of circulation as C_4AF, thereby diminishing the amount of C_3A, and (2) by decreasing the CaO/SiO_2 ratio. Notice these facts in the analyses in Table 10.6. Thus low-heat-of-setting cement is used in the construction of all large dams to avoid cracking the structure from heat stresses during setting and cooling. As an additional safeguard, the structures are cooled during setting by circulating cold water through lightweight 2.5-cm pipes, placed in the concrete mass.[13] Tables 10.9 and 10.10 present further facts regarding the functions of the different compounds in

[9]Swayze, *Am. J. Sci.* 244 (1) 63 (1946).

[10]The Ternary System: $CaO·Al_2O_3·SiO_2$, *Am. J. Sci.* 39 1–79 (1915).

[11]For hydration studies see Lea, *op. cit.*, Chap. 9.

[12]Woods, Steinour, and Strake, Effect of Composition of Portland Cement on Heat Evolved during Hardening, *Ind. Eng. Chem.* 24 1207 (1932); Bogue and Lerch, Hydration of Portland Cement Compounds, *J. Res. Natl. Bur. Stand.* 12 645 (1934).

[13]Robertson, Boulder Dam, *Ind. Eng. Chem.* 27 242 (1935).

Table 7.8 Heat of Hydration (in joules per gram)

Compound	Days				
	3	7	28	90	365
C_4AF	290	495	495	416	377
C_3A	888	1557	1378	1302	1168
C_2S	50	42	105	176	222
C_3S	243	222	377	435	490

SOURCE: *Proc. Am. Soc. Test. Mater* 50 1235 (1950).

Table 7.9 Strength Contribution of Various Compounds in Portland Cement
(The Relative Strengths Are the Apparent Relative Contributions of Equal Weights of the Compounds Listed)

1 day	$C_3A > C_3S > C_4AF > C_2S$
3 days	$C_3A > C_3S > C_4AF > C_2S$
7 days	$C_3A > C_3S > C_4AF > C_2S$
28 days	$C_3A > C_3S > C_4AF = C_2S$
3 months	$C_2S > C_3S = C_3A = C_4AF$
1 year	$C_2S > C_3S > C_3A = C_4AF$
2 years	$C_2S > C_3S > C_4AF > C_3A$

SOURCE: Steinour, Chemistry of Cement, *Portland Cement Assoc. Res. Develop. Lab. Develop. Dept. Bull.* 130; *J. Portland Cement Assoc. Res. Develop. Lab.* 3 (2) 2–11 (1961).

Table 7.10 Function of Compounds

Compound	Function
C_3A	Causes set but needs retardation (by gypsum)
C_3S	Responsible for early strength (at 7 or 8 days)
C_2S and C_3S	Responsible for final strength (at 1 year)
Fe_2O_3, Al_2O_3, Mg, and alkalies	Lower clinkering temperature

the setting and hardening of cement. To hold up the "flash set" caused by C_3A, the gypsum added as a retarder causes the formation of $C_3A \cdot 3CaSO_4 \cdot 31H_2O$.

Admixtures (additives to cement for concrete formulations) extend the supply of cement and add other important properties. These usually give specific results from individual additions. One important group is the superplasticizer naphthalene derivatives.[14] Calcium nitrite may be added to inhibit the corrosion of steel reinforcing bars in concrete.[15]

[14] *Chem. Week* 126 (11) 45 (1980).

[15] *Chem. Week* 130 (5) 21 (1982).

Concrete based on cement is broadening in application and increasing in quantity each year. Low-heat-hardening, quick or retarded hardening, low and high density prestressed concrete beams give greater strength and save steel. The Portland Cement Association, which has offices in many cities, will furnish extensive data on uses.

OTHER CEMENTS

For many corrosive conditions portland cement is unsuitable. Hence many special cements have been developed, of which some are industrially important. The types of special cements based on organic plastics, known as *adhesives*, are presented in Chap. 25, along with glues.

POZZOLANS. Since the beginning of the Christian era, the Italians have successfully employed pozzolan cement, made by grinding 2 to 4 parts of a pozzolan with 1 part of hydrated lime. A pozzolan is a material which is not cementitious in itself but which becomes so upon admixture with lime. The early strength of such a cement is lower than that of portland cement, but within a year the strengths are equal. The advantage of this cement is that it resists the corrosive action of saline solutions and seawater much better than does portland cement.

HIGH ALUMINA CEMENTS. High-alumina cement, essentially a calcium aluminate cement, is manufactured by fusing a mixture of limestone and bauxite, the latter usually containing iron oxide, silica, magnesia, and other impurities. It is characterized by a very rapid rate of development of strength and superior resistance to seawater and sulfate-bearing water.

SILICATE CEMENTS. Silica-filled, chemically setting silicate cements withstand all concentrations of inorganic acids except hydrofluoric. They are not suitable at pH values above 7 or in the presence of crystal-forming systems. Usually 2 parts by weight of finely divided silica powder is used to 1 part of sodium silicate (35 to 40°Bé). Two typical applications are the joining of bricks in chromic acid reaction tanks and in alum tanks.

SULFUR CEMENTS. Since 1900, sulfur cements have been available commercially as simple mixtures of fillers, and since 1930, as homogeneous plasticized filled sulfur ingots possessing low coefficients of expansion. Sulfur cements are resistant to nonoxidizing acids and salts but should not be used in the presence of alkalies, oils, greases, or solvents. The crystalline change in sulfur structure at 93°C limits their use. Thiokol-plasticized silica-filled sulfur cements have been accepted as a standard material for joining bricks, tile, and cast-iron pipe.

POLYMER CONCRETE. Polymer concretes are really polymer-bonded concretes and usually contain no portland cement. These products consist of aggregate plus resins such as epoxy, methyl methacrylate, or polyester. Each of the resins imparts specific properties to the concrete such as rapid curing, corrosion resistance, or high compressive strength. As yet, these concretes are much higher in price than regular portland cement concrete, but as specialty products for specific uses they are finding a market.[16]

MAGNESIUM OXYCHLORIDE CEMENT. This cement, discovered by the French chemist Sorel and sometimes called *Sorel's* cement, is produced by the exothermic action of a 20% solution

[16] *Chem. Week* 129 (21): 81 (1981).

f magnesium chloride on a blend of magnesia obtained by calcining magnesite and magnesia btained from brines

$$3MgO + MgCl_2 + 11H_2O \rightarrow 3MgO \cdot MgCl_2 \cdot 11H_2O$$

he resulting crystalline oxychloride ($3MgO \cdot MgCl_2 \cdot 11H_2O$) contributes the cementing ction to the commercial cements. The product is hard and strong but is attacked by water, hich leaches out the magnesium chloride. Its main applications are as a flooring cement ith an inert filler and a coloring pigment, and as a base for such interior floorings as tile and rrazzo. It is strongly corrosive to iron pipes in contact with it. Sand and wood pulp may be dded as fillers. The expense of these cements restricts their use to special purposes. They do ot reflect sound. They can be made sparkproof and as such have been widely employed in rdnance plants. The magnesia used may contain small amounts of calcium oxide, calcium ydroxide, or calcium silicates, which during the setting process increase the volume changes, hus decreasing strength and durability. To eliminate this time effect, hydrated magnesium ulfate ($MgSO_4 \cdot 7H_2O$) or 10% finely divided metallic copper is added to the mixture. The se of copper powder not only prevents excessive expansion, but greatly increases water resisance, adhesion, and dry and wet strength over that of ordinary magnesium oxychloride ement. Such a product even adheres in thin layers to concrete and serves to seal cracks herein.

IME

ISTORICAL. The manufacture of lime and its application can be traced back to the Roman, reek, and Egyptian civilizations, but the first definite written information concerning lime as handed down from the Romans. In his book "De Architectura," Marcus Pollio, a celerated engineer and architect who lived during the reign of Augustus (27 B.C. to A.D. 14), eals quite thoroughly with the use of lime for mortar involved in the construction of harbor orks, pavements, and buildings. In colonial America the crude burning of limestone was one f the initial manufacturing processes engaged in by the settlers; they used "dugout" kilns uilt of ordinary brick or masonry in the side of a hill, with a coal or wood fire at the bottom, nd a firing time of 72 h. These kilns can still be seen in many of the older sections of the ountry. It was not until recent years that, under the influence of chemical engineering esearch, the manufacture of lime developed into a large industry under exact technical control, resulting in uniform products at lower cost.

SES AND ECONOMICS. Lime itself may be used for medicinal purposes, insecticides, plant nd animal food, gas absorption, precipitation, dehydration, and causticizing. It is employed s a reagent in the sulfite process for papermaking, dehairing hides, the manufacture of high-grade steel and cement, water softening, recovery of by-product ammonia, and the manufacture of soap, rubber, varnish, refractories, and sand-lime bricks. Lime is indispensable for use with mortar and plaster and serves as a basic raw material in the production of calcium alts and for improving the quality of certain soils. Either directly or indirectly, limestone nd lime are employed in more industries than any other natural substance. Lime production as 18.3×10^6 t in 1972 with a value of $341.1 million. Production for 1979 was 19×10^6.

Lime is usually sold as a high-calcium quicklime containing not less than 90 percent CaO nd from 0 to 5 percent magnesia; small percentages of calcium carbonate, silica, alumina nd ferric oxide are present as impurities. The suitability of lime for any particular use

depends on its composition and physical properties, all of which can be controlled by the selection of the limestone and the details of the manufacturing process. Much lime must be finely ground before use.[17]

Depending on composition, there are several distinct types of limes. Hydraulic limes are obtained from the burning of limestone containing clay, and the nature of the product obtained after contact with water varies from putty to set cement. High-calcium-content limes harden only with the absorption of carbon dioxide from the air, which is a slow process. hydraulic limes also harden slowly, but they can be used under water. For chemical purposes high-calcium is required, except for the sulfite paper process, where magnesian lime works better. Although in many sections of the country high-calcium lime is preferred by the building industry for the manufacture of mortar lime plaster, there are places where limestone containing magnesium is burned or where even dolomitic stone is calcined. Typical compositions of such stones are from 35 to 45% CaO and from 10 to 25% MgO. These products, called *magnesian* limes, or dolimes,[18] are favored by some plasterers, who claim they work better under the trowel. In the metallurgical field, "refractory lime," as dead-burned dolomite or as raw dolomite, is employed as a refractory patching material in open-hearth furnaces; it is applied between heats to repair scored and washed spots on the bottom of the furnace. *Hydrated lime* is finding increased favor in the building trades over the less stable quicklime, despite its increased weight. Quicklime is almost invariably slaked or hydrated before use. Because of the better slaking and the opportunity to remove impurities, factory hydrate is purer and more uniform than slaked lime prepared on the job.

MANUFACTURE. Lime has always been a cheap commodity because limestone deposits are readily available in so many sections of the United States. It is produced from limestone near centers of consumption so that freight costs are low. The carbonates of calcium and magnesium are obtained from deposits of limestone, marble, chalk, dolomite, or oyster shells. For chemical usage, a rather pure limestone is preferred as a starting material because of the high-calcium lime that results. Quarries are chosen which furnish a rock that contains as impurities low percentages of silica, clay, or iron. The lumps sometimes found in "overburned" or dead-burned lime result from changes in the calcium oxide itself, as well as from certain impurities acted upon by excess heat, recognized as masses of relatively inert, semivitrified material. On the other hand, it often happens that rather pure limestone is calcined insufficiently, and lumps of calcium carbonate are left in the lime. This lime is called "underburned" lime.

The reactions involved are:

CALCINATION

$$CaCO_3(c) \rightleftharpoons CaO(c) + CO_2(g) \qquad \Delta H_{1200-1300^\circ C} = +4 \text{ GJ t of lime produced}$$

HYDRATION

$$CaO(c) + H_2O(l) \rightarrow Ca(OH)_2(c) \qquad \Delta H = -66.5 \text{ kJ}$$

During calcination the volume contracts, and during hydration it swells. For calcination the average fuel ratios, using bituminous coal, are 3.23 kg of lime for 1 kg of coal in shaft kilns

[17]Perry, p. 8-50.

[18]To prevent "popping out" the MgO must be completely hydrated, e.g., by steam hydration at 160°C and under such pressure as 413 kPa.

and 3.37 kg in rotary kilns. As is shown above, the calcination reaction is reversible. Below 650°C the equilibrium decomposition pressure of CO_2 is quite small. Between 650 and 900°C the decomposition pressure increases rapidly and reaches 101 kPa at about 900°C.[19] In most operating kilns the partial pressure of CO_2 in the gases in direct contact with the outside of the lumps is less than 101 kPa; therefore initial decomposition may take place at temperatures somewhat less than 900°C. The decomposition temperature at the center of the lump is probably well above 900°C, since there the partial pressure of the CO_2 not only is equal to or near the total pressure, but also must be high enough to cause the gas to move out of the lump, where it can pass into the gas stream. The total *heat* required for *calcining* per ton of lime produced may be divided into two parts: sensible heat to raise the rock to decomposition temperature, and latent heat of dissociation. Theoretical heat requirements per metric ton of lime produced, if the rock is heated only to a calcining temperature of 900°C, are approximately 1.4 GJ for sensible heat and 2.7 GJ for latent heat. Actual calcining operations, because of practical considerations, e.g., lump size and time, require that the rock be heated to between 1200 and 1300°C, thereby increasing sensible-heat requirements by about 370 kJ. Thus practical heat requirements are approximately 4 GJ/t of lime produced in a vertical kiln. About 40 percent is sensible heat; the rest is latent heat of decomposition.

The sequence of steps connected with manufacturing in the kiln shown in Figs. 10.3 and 7.4 are:

Blasting down of limestone from a quarry face or occasionally from underground veins.
Transportation from the quarry to mills, generally by an industrial railroad.

[19]ECT, 3d ed., vol. 14, 1981, pp. 615–646.

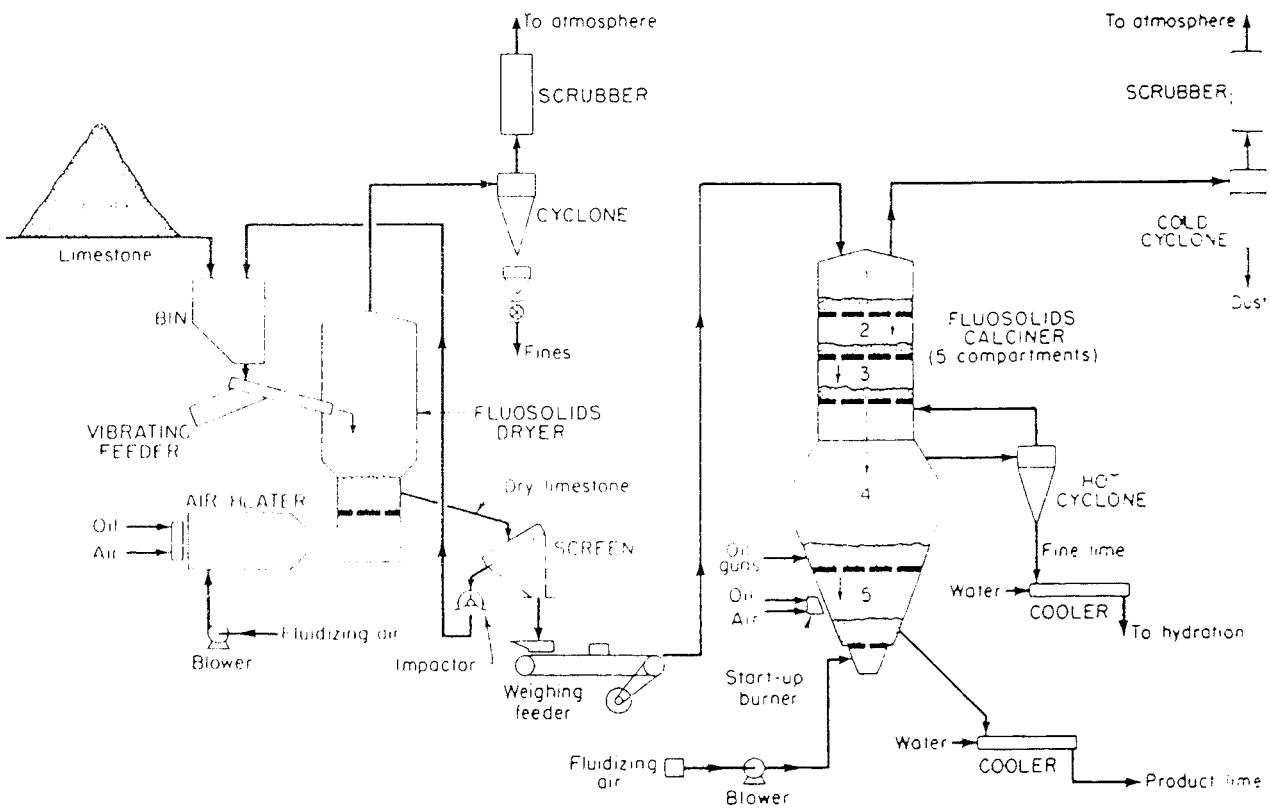

Fig. 7.3. Dorrco FluoSolids system for producing lime from pulverized limestone or calcium carbonate sludge. This is a five-compartment reactor as labeled. *(Dorr-Oliver, Inc.)*

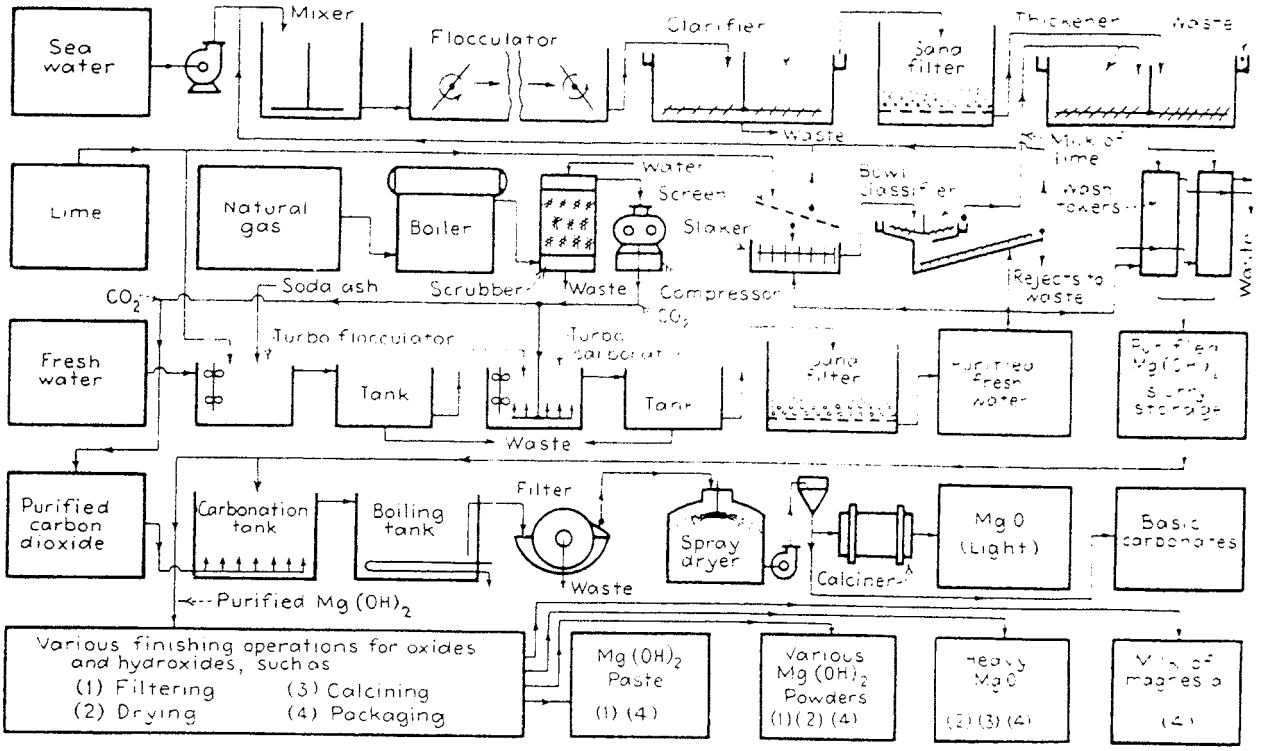

Fig. 7.4. Purified magnesium compounds from seawater at South San Francisco. *(Merck & Co.)*

Crushing and sizing of the stone in jaw and gyratory crushers.[20]

Screening to remove various sizes (e.g., a 10- to 20-cm stone implies that all pieces passing a 10-cm screen and retained on an 20-cm screen have been separated out).

Carting of large stones to top of vertical kilns.

Conveying of small rocks to a rotary kiln.

Conveying of fines to a pulverizer to make powdered limestone for agricultural and other demands.

Burning of limestone according to size, in vertical kilns to give lump lime, or in horizontal rotary kilns to furnish fine lime.

Packaging of the finished lime in barrels (80 or 120 kg) or sheet-iron drums or conveying it to a hydrator.

Hydration of the lime.

Packaging of slaked lime in 25-kg paper bags.

Almost all lime produced in the United States is calcined in *rotary kilns*. These kilns may have a capacity of up to 1600 t/day. In 1965 the largest rotary kiln would only produce 600 t/day. The diameters are usually about 5 m with lengths of 45 to 60 m. The diameter-to-length ratio is 1:10 to 1:12.

The exterior of the rotary kiln is heavy steel and the interior is lined with refractory brick. The kilns have a slope of 4 percent and rotate counterclockwise at a speed of 0.6 to 2 rpm. The limestone is preheated to reduce fuel consumption and may be as hot as 980°C when it enters the kiln. Heat for the preheater is furnished by the hot air and gases from the kiln. These kilns operate on fines or small lumps of limestone or marble, or moist precipitated calcium carbonate sludge, any of which would block the efficient and uniform burning of the fuel in a vertical kiln. Rotary kilns have the highest capacity and produce lime of the most

[20]Perry, p. 8-16.

uniform quality but require the greatest capital investment, have a high energy consumption, and need very expensive dust-collecting systems.[21]

Vertical kilns have hundreds of designs and are used largely outside of the United States as American consumers prefer the better quality of lime produced by the rotary kilns. The main characteristic that all vertical kilns have in common is four imaginary zonal sections: (1) storage, (2) preheating, (3) calcining, and (4) cooling. The limestone is charged into the top of the kiln and cooled lime is discharged at the bottom. An improved vertical kiln is the Maerz-Ofenbau double shaft regenerative kiln,[22] which increases production and uses less energy. The only one in operation in the United States is at Douglas, Ariz. and is heated with natural gas. This kiln consists of two shafts connected at the lower third of the structure. The fuel is fed alternately to the shafts at 10- to 12-min intervals. Approximately 24 h elapse until the cooled lime is removed. This alternate calcining prevents overburning of the lime and produces lime equal in quality to that produced by rotary kilns but uses only about half the fuel.

Dorrco FluoSolids kiln is a vertical kiln but operates on a different principle. The feed is granular (0.225 to 2.4 mm) material and fluidized by a carefully controlled air and exhaust-gas mixture. This is an extension of the fluidized bed reactor used so widely in the petroleum industry.

GYPSUM

Gypsum is a mineral that occurs in large deposits throughout the world.[23] It is hydrated calcium sulfate, with the formula $CaSO_4 \cdot 2H_2O$. When heated slightly, the following occurs:

$$CaSO_4 \cdot 2H_2O(c) \rightarrow CaSO_4 \cdot \tfrac{1}{2}H_2O(c) + 1\tfrac{1}{2}H_2O(g) \qquad \Delta H_{25°C} = +69 \text{ kJ}$$

If the heating is at a higher temperature, gypsum loses all its water and becomes anhydrous calcium sulfate, or *anhydrite*. Calcined gypsum (the half water salt) can be made into wall plaster by the addition of a filler material such as asbestos, wood pulp, or sand. Without additions, it is plaster of paris and is used for making casts and for plaster; it is hydraulic and hardens under water, but is also slightly soluble in water, hence must not be used in moist exposures.

CALCINATION OF GYPSUM. The usual method of calcination of gypsum consists in grinding the mineral and placing it in large calciners holding 9 to 22 t. The temperature is raised to about 120 to 150°C with constant agitation to maintain a uniform temperature. The material in the kettle, known to the public as *plaster of paris* and to the manufacturer as *first-settle plaster*, may be withdrawn and sold at this point, or it may be heated further to 190°C to give a material known as *second-settle plaster*. First-settle plaster is approximately the half hydrate $CaSO_4 \cdot \tfrac{1}{2}H_2O$, and the second form is anhydrous. Practically all gypsum plaster sold is in the form of first-settle plaster mixed with sand or wood pulp. The second form is used

[21]ECT, 3d ed., vol. 14, 1981, p. 362; Robertson, U.S. Lime Division Expands Its Nelson, Arizona Plant, *Rock Prod.* 81 (10) 59 (1978).

[22]Robertson, Double-Shaft Regenerative Kiln, *Rock Prod.* 83 (10) 50 (1980).

[23]ECT, 3d ed., vol. 4, 1978, pp. 437–448.

in the manufacture of plasterboard and other gypsum products. Gypsum may also be calcined in rotary kilns similar to those used for limestone.

HARDENING OF PLASTER. This hardening of plaster is essentially a hydration chemical conversion, as represented by the equation

$$CaSO_4 \cdot \tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad \Delta H = -2.9 \text{ kJ}$$

This equation is the reverse of that for the dehydration of gypsum. The plaster sets and hardens because the liquid water reacts to form a solid, crystalline hydrate. Hydration with liquid water takes place at temperatures below about 99°C and thus the gypsum must be heated above 99°C for practical dehydration. Commercial plaster usually contains some glue in the water used or a material such as hair or tankage from the stockyards to retard the setting time in order to give the plasterer opportunity to apply the material.

MISCELLANEOUS CALCIUM COMPOUNDS

CALCIUM CARBONATE. Calcium carbonate is a very widely used industrial chemical, in both its pure and its impure state. As marble chips, it is sold in many sizes as a filler for artificial stone, for the neutralization of acids, and for chicken grit. Marble dust is employed in abrasives and in soaps. Crude, pulverized limestone is used in agriculture to "sweeten" soils in large tonnage. Some pulverized and levigated limestone, to replace imported chalk and whiting, is manufactured quite carefully from very pure raw material and is finding acceptance.[24] *Whiting* is pure, finely divided calcium carbonate prepared by wet grinding and levigating natural chalk. Whiting mixed with 18% boiled linseed oil yields *putty*, which sets by oxidation and by formation of the calcium salt. Much whiting also is consumed in the ceramic industry. Precipitated, or artificial, whiting arises through precipitation, e.g., from reacting a boiling solution of calcium chloride with a boiling solution of sodium carbonate or passing carbon dioxide into a milk-of-lime suspension. Most of the latter form is used in the paint, rubber, pharmaceutical, and paper industries.

CALCIUM SULFIDE. Calcium sulfide is made by reducing calcium sulfate with coke. Its main use is as a depilatory in the tanning industry and in cosmetics. In a finely divided form it is employed in luminous paints. Polysulfides, such as CaS_2 and CaS_5, made by heating sulfur and calcium hydroxide, are consumed as fungicides.

HALIDE SALTS. Calcium chloride is obtained commercially as a by-product of chemical manufacture and from natural brines which contain more or less magnesium chloride. In 1980 730,000 t was sold. Its main applications are to lay dust on highways (because it is deliquescent and remains moist), to melt ice and snow on highways in winter, to thaw coal, in oil and gas well fluids, and as an antifreeze for concrete.

Calcium bromide and iodide have properties similar to those of the chloride. They are prepared by the action of the halogen acids on calcium oxide or calcium carbonate. They are sold as hexahydrates for use in medicine and photography. Calcium fluoride occurs naturally

[24]Rose, *Condensed Chemical Dictionary*, 7th ed. New York, Reinhold, 1966.

as a fluorspar (Chap. 20). Calcium hypochlorite [$Ca(OCl)_2$] is prepared by the action of chlorine on calcium hydroxide (Chap. 10). Its primary use is for swimming pool sanitation.

CALCIUM ARSENATE. Calcium arsenate is produced by the reaction of calcium chloride, calcium hydroxide, and sodium arsenate or lime and arsenic acid:

$$2CaCl_2(aq) + Ca(OH)_2(c) + 2Na_2HAsO_4(aq) \rightarrow Ca_3(AsO_4)_2(c) + 4NaCl(aq) + 2H_2O(l) \qquad \Delta H = -27.8 \text{ kJ}$$

Some free lime is usually present. Calcium arsenate is used extensively as an insecticide and as a fungicide.

CALCIUM ORGANIC COMPOUNDS. Calcium acetate and lactate are prepared by the reaction of calcium carbonate or hydroxide with acetic or lactic acid. The *acetate* was formerly pyrolyzed in large amounts to produce acetone, but now it is employed largely in the dyeing of textiles. The *lactate* is sold for use in medicines and in foods as a source of calcium; it is an intermediate in the purification of fermentation lactic acid. *Calcium soaps* such as stearate, palmitate, and the abietate are made by the action of the sodium salts of the acids on a soluble calcium salt such as the chloride. These soaps are insoluble in water but are soluble in hydrocarbons. Many of them form jellylike masses, which are constituents of greases. These soaps are used mainly as waterproofing agents.

MAGNESIUM COMPOUNDS[25]

Magnesium is one of the most widely distributed elements, occupying 1.9 percent of the earth's crust. It occurs usually in the chloride, silicate, hydrated oxide, sulfate, or carbonate, in either a complex or in simple salts. Magnesium metal first became available commercially shortly before 1914, when the Germans initiated production, using magnesium chloride from the Stassfurt deposits as the raw material. Table 7.11 gives recent production figures for magnesium and its compounds.

RAW MATERIALS AND USES. Important domestic sources of magnesium salts are seawater, certain salt wells, bitterns from sea brine, salines, dolomite, and magnesite ($MgCO_3$). Magnesium compounds are used extensively for refractories and insulating compounds, as well as in the manufacture of rubber, printing inks, pharmaceuticals, and toilet goods.

Magnesium oxide is finding new important uses in air pollution control systems for the removal of sulfur dioxide from stack gases.[26] New uses for magnesium may mean major growth for this metal in the future.

MANUFACTURE. The manufacture of magnesium compounds from salines has long been successful in Germany. As a result of thorough physical and chemical study, the International Minerals and Chemical Corp. is making magnesium chloride from langbeinite, crystallizing

[25]ECT, 3d ed., vol. 14, 1981, pp. 615–646.

[26]Shah, MgO Absorbs Stack Gas SO_2, *Chem. Eng.* 79 (14) 80 (1974).

***Table* 7.11** Magnesium and Magnesium Compounds Statistics 1981 (thousands of metric tons and thousands of dollars)

	Quantity	Value
Used in the United States		
Caustic-calcined and specified (USP and technical) magnesia	145	58,420
Refractory magnesia	360	146,963
Dead-burned dolomite	395	23,789
U.S. Production		
Primary magnesium	130	
Secondary magnesium	42	
World Production		
Primary magnesium	298	

SOURCE: *Minerals Yearbook 1981*, vol. 1, Dept. of the Interior, 1982, pp. 298, 555, 565.

out carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). This double salt is decomposed to furnish magnesium chloride.

The production of magnesium compounds by separation from aqueous solutions may be divided into four processes:

1. Manufacture from seawater without evaporation, using seawater and lime as the principal raw materials. This is done by Dow Chemical Co. at Freeport and Velasco, Tex.,[27] and by Merck & Co. at South San Francisco (Fig. 7.4). The Dow Chemical Co. of Freeport and Velasco, Tex., manufactures magnesium hydrate, which is dissolved in 10% hydrochloric acid to furnish a solution of magnesium chloride. This is concentrated in direct-fired evaporators, followed by shelf dryers, producing 76% magnesium chloride ready to be delivered to electrolytic cells to make metallic magnesium (Chap. 11).
2. Manufacture from bitterns or mother liquors from the solar evaporation of seawater for salt.
3. Manufacture from dolomite and seawater, with factories operating at Moss Landing, Calif., by Kaiser Chemical Division, as depicted by the flowchart in Fig. 10.5. At Pascagoula, Miss. Corning Glass Works obtains magnesium salts from similar sources.
4. Manufacture from deep-well brines. Production is being increased by Dow Chemical Co. with Michigan brines, analyzing 20.7% $CaCl_2$, 3.9% $MgCl_2$, 5.73% NaCl. The small amount of bromine is freed by chlorine and, following its removal, the $Mg(OH)_2$ is precipitated by pure slaked dolime (calcined dolomite). The $Mg(OH)_2$ produced is settled, filtered, and washed to provide a slurry containing 45% $Mg(OH)_2$ of high purity. This is calcined at high temperatures to produce periclase, a sintered MgO nodule used in making refractory brick.

A typical analysis of seawater is given in Table 7.12. The production of magnesium compounds from seawater is made possible by the almost complete insolubility of magnesium hydroxide in water. Success in obtaining magnesium compounds by such a process depends upon

1. Means to soften the seawater cheaply, generally with lime or calcined dolomite
2. Preparation of a purified lime or calcined dolomite slurry of proper characteristics

[27] *Chem. Week* **127** (8) 22 (1980).

3. Economical removal of the precipitated hydroxide from the large volume of water.
4. Inexpensive purification of the hydrous precipitates.
5. Development of means to filter the slimes.

The reactions are

$$MgCl_2(aq) + Ca(OH)_2(c) \rightarrow Mg(OH)_2(c) + CaCl_2(aq) \qquad \Delta H = -9.46 \text{ kJ}$$

$$MgSO_4(aq) + Ca(OH)_2(c) + 2H_2O(l) \rightarrow Mg(OH)_2(c) + CaSO_4 \cdot 2H_2O(c) \qquad \Delta H = -13.3 \text{ kJ}$$

Figure 7.5 shows a flowchart of magnesium products from seawater. Figure 7.4 presents a flowchart for producing such fine chemicals and pharmaceuticals as milk of magnesia and several basic magnesium carbonates such as $3MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ for tooth powders and antacid remedies, for coating table salt to render it noncaking, and for paint fillers. Certain of these basic magnesium compounds are also employed with rubber accelerators. Where calcined dolomite is used instead of calcium carbonate, only about one-half of the magnesia must come from the magnesium salts in the seawater.[28] Consequently, the size of the plant is much smaller and the cost of production probably lower. The $Mg(OH)_2$ may be calcined at about 700°C to active, chemical MgO, or at about 1475 to 1650°C to periclase MgO. This $Mg(OH)_2$ is quite different from the slow-settling $Mg(OH)_2$ precipitated by a soluble alkali or by milk of lime.

The reactions, as illustrated in the flowchart in Figs. 7.4 and 7.5, are the following

CALCINATION

$$2CaMg(CO_3)_2(c) \rightarrow 2CaO(c) + 2MgO(c) + 4CO_2(g) \qquad \Delta H = +610.9 \text{ kJ}$$

SLAKING

$$2CaO(c) + 2MgO(c) + 4H_2O(l) \rightarrow 2Ca(OH)_2(c) + 2Mg(OH)_2(c) \qquad \Delta H = -[\text{illegible}] \text{ kJ}$$

PRECIPITATION

$$2Ca(OH)_2(c) + 2Mg(OH)_2(c) + MgCl_2(aq) + MgSO_4(aq) + 2H_2O(l) \rightarrow 4Mg(OH)_2(c) + CaCl_2(aq) + CaSO_4 \cdot 2H_2O(s) \qquad \Delta H = -22.6 \text{ kJ}$$

CALCINATION

$$4Mg(OH)_2(c) \rightarrow 4MgO(c) + 4H_2O(g) \qquad \Delta H = +248.5 \text{ kJ}$$

HYDROCHLORINATION

$$Mg(OH)_2(c) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l) \qquad \Delta H = -44.7 \text{ kJ}$$

only about 7 percent of the slaked calcined dolomite is needed for softening the seawater; the rest is used for precipitating crystalline $Mg(OH)_2$ which is settled, filtered, and washed. This hydroxide is converted to other products.

[28]Seawater normally has 2.2 g/L of equivalent MgO, actually present as $MgCl_2$ and $MgSO_4$. Hence 1 t of MgO theoretically requires 375 m^3 of seawater. Based on a 70 percent yield, about 538 m^3 would be pumped if all the magnesia came from seawater, or about half the amount if dolomite were used.

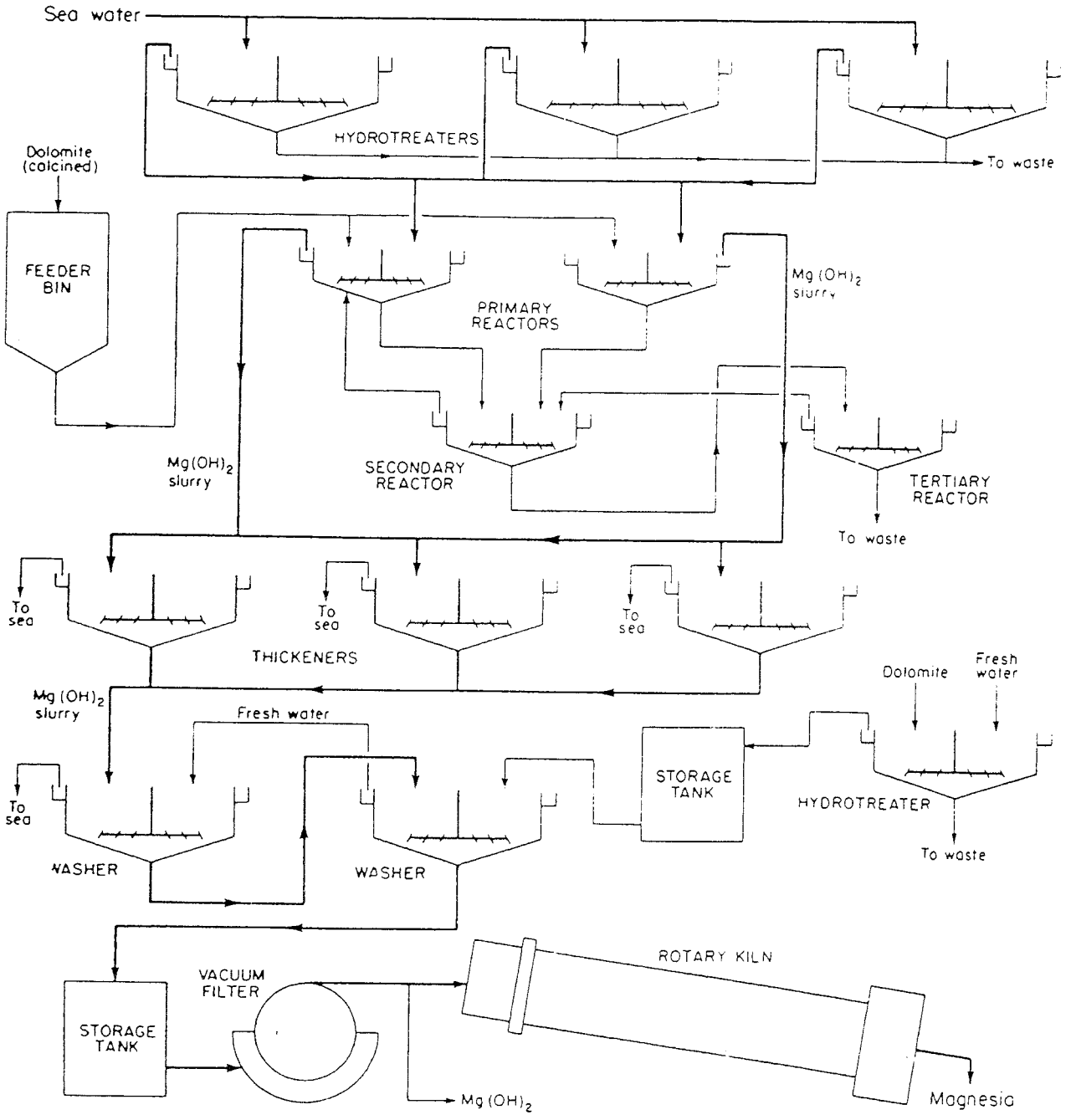

Fig. 7.5. Flowchart for $Mg(OH)_2$ from seawater and dolomite. *(Kaiser Chemical Co., Moss Landing, Calif.)*

Table 7.12 Composition of Seawater (in grams per liter of sp gr 1.024)

NaCl	27.319	$Ca(HCO_3)_2$	0.178
$MgCl_2$	4.176	K_2SO_4	0.869
$MgSO_4$	1.668	B_2O_3	0.029
$MgBr_2$	0.076	SiO_2	0.008
$CaSO_4$	1.268	Iron and alumina (R_2O_3)	0.022

MAGNESIUM CARBONATES. These vary from dense $MgCO_3$ used in magnesite bricks to the very low density $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ and $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$ once employed for insulation. There are also other basic carbonates on the market with variations in adsorptive index and apparent density. Many of these are employed as fillers in inks, paints, and varnishes (see Fig. 7.4 for manufacture).

OXIDES AND HYDROXIDE OF MAGNESIUM. On heating magnesium carbonate or hydroxide, magnesium oxide (MgO) is formed. This oxide has many uses, e.g., in the vulcanization of rubber, as a material for making other magnesium compounds, as an insulating material, as a refractory material, and as an abrasive. The magnesium hydroxide is principally made directly from seawater, as Figs. 7.4 and 7.5 show. The seawater is screened and pumped to a battery of three 38-m-diameter concrete hydrotreaters. Here enough calcined dolomite is added (not shown in the figure) to pretreat or soften the seawater by precipitating carbonates, which are removed by rakes. The softened seawater flows to two primary reactors 25 m in diameter into which is fed the main addition of calcined dolomite to precipitate the $Mg(OH)_2$, which in a fine suspension overflows into three parallel-flow 76-m-diameter thickeners, the overflow being returned to the sea. The underflow of the two primary reactors is fed first into an 18-m-diameter secondary reactor and then into the tertiary reactor, from which the three-times-reacted residue, now largely silicious material and unreacted dolomite, is wasted. The thickened $Mg(OH)_2$ slurry from the three 76-m thickeners is united and washed with calcined-dolomite-softened fresh water in two 76-m thickeners in series. The $Mg(OH)_2$ underflow is conducted through storage to a 4- by 5.5-m rotary filter operating at about 26.7-kPa vacuum and delivering about 50% $Mg(OH)_2$. This is removed from the rotary filter and conveyed either to sale or to one of three rotary kilns operating up to 1800°C to give different grades of MgO. After purification this is the well-known milk of magnesia used in medicine. *Magnesium peroxide* is available from the reaction of magnesium sulfate and barium peroxide. It is employed as an antiseptic and a bleaching agent.

MAGNESIUM SULFATE. Magnesium sulfate is prepared by the action of sulfuric acid on magnesium carbonate or hydroxide. It is sold in many forms, one of which is the hydrate $MgSO_4 \cdot 7H_2O$, long known as *Epsom salts*. The less pure material is used extensively as sizing and as a fireproofing agent.

MAGNESIUM CHLORIDE. Magnesium chloride is made from hydrochloric acid and magnesium hydroxide as described above. The compound itself much resembles calcium chloride and has many of the same uses. In addition, it finds application in ceramics, in the sizing of paper, and in the manufacture of oxychloride cement. Its principal use is in the making of metallic magnesium.

MAGNESIUM SILICATES. A consideration of magnesium silicates includes two widely used naturally occurring compounds, asbestos and talc. Asbestos is a magnesium silicate mixed with varying quantities of silicates of calcium and iron. It is a fibrous, noncombustible mineral and is used in the manufacture of many fireproof and insulating materials. Because of the cancer-causing characteristics of its fibers, government regulations have sharply reduced its use. Talc is a rather pure magnesium silicate in the form of $3MgO \cdot 4SiO_2 \cdot H_2O$, found naturally in soapstone. It is employed as a filler in paper and plastics and in many cosmetic and toilet preparations.

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Chapter 8

Glass Industries

Glass may be defined, *physically*, as a rigid, undercooled liquid having no definite melting point and a sufficiently high viscosity (greater than 10^{12} Pa·s) to prevent crystallization; and *chemically*, as the union of the nonvolatile inorganic oxides resulting from the decomposition and fusion of alkali and alkaline earth compounds, sand, and other glass constituents, ending in a product with *random* atomic structure. Glass is a *completely vitrified* product, or at least such a product with a relatively small amount of nonvitreous material in suspension.

Glass has many uses because of its transparency, high resistance to chemical attack, effectiveness as an electrical insulator, and ability to contain a vacuum. Glass is a brittle material and characteristically exhibits compressive strength much greater than its tensile strength. Strengthening techniques, most of which involve prestressing to introduce surface compression, have been developed to the point where glass can be employed in more arduous environments than previously. Approximately 800 different glass compositions are produced, some with particular emphasis on one property and some with attention to a balanced set of properties.

HISTORICAL.[1] As in the case of many other commonplace materials of our modern civilization, the discovery of glass is very uncertain. One of the earliest references to this material was made by Pliny, who related the familiar story of how ancient Phoenician merchants discovered it while cooking a meal in a vessel placed accidentally upon a mass of trona at the seashore. The union of the sand and alkali caught the men's attention and led to subsequent efforts at imitation. As early as 600B or 5000 B.C. the Egyptians were making sham jewels of glass which were often of fine workmanship and marked beauty. Window glass is mentioned as early as A.D. 290. The hand-blown window-glass cylinder was invented by a twelfth-century monk. During medieval times Venice enjoyed a monopoly as the center of the glass industry. It was not until the fifteenth century, however, that the use of window glass became general. No glass was made in either Germany or England until the sixteenth century. Plate glass appeared as a rolled product in France in 1688.

Glassworks in the United States were founded in 1608 at Jamestown, Va., and in 1639 at Salem, Mass. For more than three centuries thereafter, the processes were practically all manual and rule of thumb. From the chemical point of view, the only major improvements during this period were confined to purifying the batch materials and increasing the fuel economy. To be sure, some relations were established between the chemical composition of glasses and their optical and other physical properties but, all in all, the industry prior to 1900 was an

[1]Shand, *Glass Engineering Handbook*, 2d ed., McGraw-Hill, New York, 1958; for an excellent general presentation, Stookey, Glass Chemistry as I Saw It, *CHEMTECH*, 1(5) 458 (1971).

art, with closely guarded secret formulas and empirical processes of manufacture based primarily upon experience.

In 1914 the Fourcault process for drawing a sheet of glass continuously was developed in Belgium. During the next 50 years engineers and scientists produced modifications of the flat-sheet drawing process aimed at reducing the optical distortion characteristic of sheet (window) glass and the cost of producing ground and polished plate glass. These efforts led to the most recent step forward in flat-glass production technology. Based on concepts patented in the United States in 1902 and 1905, a research group in England perfected the float glass process in the 1960s. Float glass has all but eliminated plate glass produced by other means and has invaded the market for window glass in a major way. Scientists and engineers entered the field in increasing numbers, and new products appeared as a result of intensive research. Automatic machines were invented to speed up production of bottles, light bulbs, etc. As a result, today the glass industry is a highly specialized field.

USES AND ECONOMICS. Glass and glassware production by types are shown in Table 8.1. The uses and applications of glass are very numerous, but some conception of the versatility of this material can be gained from a discussion of the various types, as presented in the rest of this chapter. Overall, glassmaking in the United States is about a $7000 million per year industry. Automobile glass represents almost half of the flat glass produced annually. The architectural trend is toward more glass in commercial buildings and in particular colored glass.[2]

COMPOSITION. In spite of thousands of new formulations for glass during the past 30 years, it is worthy of note that lime, silica, and soda still form over 90 percent of all the glass of the world, just as they did 2000 years ago. It should not be inferred that there have been no important changes in composition during this period. Rather, there have been minor changes in major ingredients and major changes in minor ingredients. The major ingredients are sand, lime, and soda ash, and any other raw materials may be considered minor ingredients, even though the effects produced may be of major importance. The most important factors in making glass are viscosity of molten oxides and the relation between this viscosity and composition. Table 8.2 shows the chemical composition of various glasses.

In general, commercial glasses fall into several classes.

1. ***Fused silica.*** Fused silica, or vitreous silica, is made by the high-temperature pyrolysis of silicon tetrachloride or by fusion of quartz or pure sand. It is sometimes erroneously referred to as *quartz glass* and is characterized by low expansion and a high softening point

[2]Market for Colored Glass Accelerates, *Chem. Eng. News* 48 (5) 14 (1970).

Table 8.1 Value of Glass and Glassware Shipped (in millions of dollars)

	1972	1977
Flat glass, total	937.2	1576.6
Pressed and blown glass	1267	2120.1
Glass containers	2126.5	3664.2

SOURCE: *Census of Manufacturers, 1977*, Dept. of Commerce, 1980.

***Table* 8.2** Chemical Composition of Typical Glasses (in percent)

No.*	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	As_2O_3	CaO	MgO	Na_2O	K_2O	PbO	ZnO	BaO	Sb_2O_3	LiO_2	SO_3
1	67.8		4.4			4.0	2.3	13.7	2.3						1.0
2	69.4		3.5	1.1		7.2		17.3							
3	72.5		1.4			13.3		14.0							
4	73.0		0.8			12.7	0.2	12.7							
5	71.8		1.4	0.1		8.9	3.3	14.3							0.3
6	70.6		0.8	0.1		10.6	0.1	17.0							0.8
7	72.7		0.5	0.1		13.0		13.2					0.2		0.4
8	72.0		2.1			10.2		14.9							0.8
9	72.4		0.8	0.4		5.3	3.7	17.4							
10	66.4	4.0	2.4				5.2	15.6			6.2				
11	81	12.5	2.0					4.5						1.0	
12	72.4		1.0	0.1		8.1	0.2	18.1				0.2			
13	67.2				0.5	0.9		9.5	7.1	14.8					
14	96.3	2.9	0.4												
15	100														
16	55	10	14			13	5	0.5				1			

*Notes: 1, Egyptian, 1500 B.C.; 2, Pompeian window; 3, window, American cylinder, 19th century; 4, window, Machine cylinder, 1920; 5, window, Fourcault, 1929, American; 6, window, Fourcault, European; 7, plate with SbO_2; 8, soda-lime container, American 1949; 9, electric lamp bulb; 10, Jena laboratory, before 1910; 11, Pyrex laboratory; 12, tableware—soda-lime; 13, tableware—lead crystal; 14, 96% silica, Vycor; 15, fused silica; 16, "E" glass for fibers

SOURCES 1 and 2—Blau, Chemical Trends, *Ind. Eng Chem.* 32 1429 (1940); 3-16—Scholes and Greene, *Modern Glass Practice*, Cahners, Boston, Mass., 1975

which impart high thermal resistance and permit it to be used beyond the temperature ranges of other glasses. This glass is also extraordinarily transparent to ultraviolet radiation.

2. *Alkali silicates.* Alkali silicates are the only two-component glasses of commercial importance. Sand and soda ash are simply melted together, and the products designated sodium silicates,[3] having a range of composition from $Na_2O \cdot SiO_2$ to $Na_2O \cdot 4SiO_2$. A knowledge of the equilibrium relations[4] in these two-component systems has aided the glass technologist in understanding the behavior of more complicated systems. Silicate of soda solution, also known as *water (soluble) glass*, is widely consumed as an adhesive for paper in the manufacture of corrugated-paper boxes. Other uses include fireproofing. The higher-alkaline varieties are used for laundering as detergents and as soap builders.

3. *Soda-lime glass.* Soda-lime glass constitutes 95 percent of all glass manufactured. It is used for containers of all kinds, flat glass, automobile and other windows, tumblers, and tableware. There has been a general improvement in the physical quality of all flat glass, such as increased flatness and freedom from waves and strains, but the chemical composition has not varied greatly. The composition as a rule lies between the following limits (Table 8.2): (1) SiO_2, 70 to 74%; (2) CaO, 8 to 13%; (3) Na_2O, 13 to 18%. Products of these ratios melt at relatively low temperatures. They are sufficiently viscous that they do not devitrify and yet are not too viscous to be workable at reasonable temperatures. The great improvement has been in the substitution of instrument-controlled mechanical devices for the hand operator. Similarly, in container glass, the progress has been largely of a mechanical nature. However, the influence of the liquor trade has created a tendency among manufacturers to make glassware particularly high in alumina and lime and low in alkali. This type of glass melts with more difficulty but is more chemically resistant. The color of container glass is much better than formerly because of the improved selection and purification of raw materials and the use of selenium as a decolorizer.

Applications of phase-rule[5] studies have explained many of the earlier empirical observations of the glassmaker, have led to some improvements (such as more exactness in the manufacture of soda-lime glass), and have laid the basis for new glass formulations. The phase diagrams for many systems are known and have been published, and the system Na_2O–CaO–SiO_2 has been particularly detailed.

4. *Lead glass.* By substituting lead oxide for calcium oxide in the glass melt, lead glass is obtained (see No. 13 in Table 8.2). These glasses are of very great importance in optical work because of their high index of refraction and dispersion. Lead contents as high as 92% (density 8.0, refractive index 2.2) have been made. The brilliance of good "cut glass" is due to its lead-bearing composition. Large quantities are used also for the construction of electric light bulbs, neon-sign tubing, and radiotrons because of the high electrical resistance of this glass. It is also suitable for shielding from nuclear radiation.

5. *Borosilicate glass.* Borosilicate glass usually contains about 10 to 20% B_2O_3, 80 to 87% silica, and less than 10% Na_2O. This type of glass has a low expansion coefficient, superior resistance to shock, excellent chemical stability, and high electrical resistance. The laboratory glassware made from this glass is sold under the tradename Pyrex. In recent years, however, the name Pyrex has been applied to many glass objects made from other compositions, such

[3]See Chap. 12 for fuller descriptions.

[4]Morey, *The Properties of Glass*, 2d ed., Reinhold, New York, 1954.

[5]Morey, *Data of Geochemistry*, Geological Survey Paper 440L, U.S. Govt. Printing Office, 1964; Shahid and Glasser, Phase Equilibrium in the System Na_2O-CaO-SiO_2, *Phys. Chem. Glasses* **12** 50 (1971).

as alumino-silicate glass for top-of-the-stove ware. Uses of borosilicate glasses, in addition to laboratory ware, are high-tension insulators and washers, pipelines, and telescope lenses such as the 500-cm disk at Mt Palomar

6. *Special glasses.* Colored and coated, opal, translucent, safety, optical, photochromic glasses, and glass ceramics are special glass. All of these have varying compositions depending upon the final product desired

7. *Glass fibers.* Glass fibers are produced from special glass compositions that are resistant to weather conditions. The very large surface area of the fibers makes them vulnerable to attack by moisture in the air. This glass is low in silica, about 55%, and low in alkali (see No. 16, Table **8**.2).

RAW MATERIALS.[6] In order to produce these various glasses, large tonnages of glass sand are used in the United States each year. Soda ash, salt cake, and limestone or lime are required to flux this silica. In addition, there is heavy consumption of lead oxide, pearl ash (potassium carbonate), saltpeter, borax, boric acid, arsenic trioxide, feldspar, and fluorspar, together with a great variety of metallic oxides, carbonates, and the other salts required for colored glass. In finishing operations, such diverse products as abrasives and hydrofluoric acid are consumed.

Sand for glass manufacture should be almost pure quartz. A glass-sand deposit has, in many cases, determined the location of a glass factory. Its iron content should not exceed 0.45% for tableware or 0.015% for optical glass, as iron affects the color of most glass adversely.

Soda (Na_2O) is principally supplied by dense soda ash (Na_2CO_3). Other sources are sodium bicarbonate, salt cake, and sodium nitrate. The latter is useful in oxidizing iron and in accelerating the melting. The important sources of *lime* (CaO) are limestone and burnt lime from dolomite ($CaCO_3 \cdot MgCO_3$), the latter introducing MgO into the batch.

Feldspars have the general formula $R_2O \cdot Al_2O_3 \cdot 6SiO_2$, where R_2O represents Na_2O or K_2O or a mixture of these two. They have many advantages over most other materials as a source of Al_2O_3, because they are cheap, pure, and fusible and are composed entirely of glass-forming oxides. Al_2O_3 itself is used only when cost is a secondary item. Feldspars also supply Na_2O or K_2O and SiO_2. The alumina content serves to lower the melting point of the glass and to retard devitrification.

Borax, as a minor ingredient, supplies glass with both Na_2O and boric oxide. Though seldom employed in window or plate glass, borax is now in common use in certain types of container glass. There is also a high-index borate glass that has a lower dispersion value and a higher refractive index than any glass previously known and is valuable as an optical glass. Besides its high fluxing power, borax not only lowers the expansion coefficient but also increases chemical durability. Boric acid is used in batches where only a small amount of alkali is wanted. Its price is about twice that of borax.

Salt cake, long accepted as a minor ingredient of glass, and also other sulfates such as ammonium and barium sulfate, are encountered frequently in all types of glass. Salt cake is said to remove the troublesome scum from tank furnaces. Carbon should be used with sulfates to reduce them to sulfites. *Arsenic trioxide* may be added to facilitate the removal of bubbles. *Nitrates* of either sodium or potassium serve to oxidize iron and make it less noticeable in the finished glass. Potassium *nitrate* or carbonate is employed in many better grades of table, decorative, and optical glass.

[6]ECT, 3d ed., vol. 11, 1980, pp. 807–880.

Cullet is crushed glass from imperfect articles, trim, and other waste glass. It facilitate melting and utilizes waste material. It may be as low as 10 percent of the charge or as hig as 80 percent.

Refractory blocks for the glass industry have been developed especially because of th severe conditions encountered. *Sintered* zircon, alumina, mullite, mullite-alumina and *elec trocast* zirconia-alumina-silica, alumina, and chrome-alumina are typical of those for glas tanks. See electrocast refractories, Chap. 6. The latest practice in regenerators utilizes basi refractories because of the alkali dust and vapors. Furnace operating temperatures are limite mainly by silica-brick crowns, which are economical to use in the industry.

CHEMICAL REACTIONS. The chemical reactions involved may be summarized

$$Na_2CO_3 + aSiO_2 \rightarrow Na_2O \cdot aSiO_2 + CO_2 \quad (1$$

$$CaCO_3 + bSiO_2 \rightarrow CaO \cdot bSiO_2 + CO_2 \quad (2$$

$$Na_2SO_4 + cSiO_2 + C \rightarrow Na_2O \cdot cSiO_2 + SO_2 + CO \quad (3$$

The last reaction may take place as in equations (4) or (5), and (6):

$$Na_2SO_4 + C \rightarrow Na_2SO_3 + CO \quad (4$$

$$2Na_2SO_4 + C \rightarrow 2Na_2SO_3 + CO_2 \quad (5$$

$$Na_2SO_3 + cSiO_2 \rightarrow Na_2O \cdot cSiO_2 + SO_2 \quad (6$$

The ratios Na_2O/SiO_2 and CaO/SiO_2 are not molar ratios. The ratio may be of the type $Na_2O/1.8SiO_2$, for example. In an ordinary window glass the molar ratios are *approximately* 1.5 mol Na_2O, 1 mol CaO, and 5 mol SiO_2. Other glasses vary widely (Table 8.2).

Typical manufacturing sequences can be broken down into the following.

Transportation of raw materials to the plant.
Sizing of some raw materials.
Storage of raw materials.
Conveying, weighing, and mixing raw materials, and feeding them into the glass furnace.
Burning of the fuel to secure temperature needed for glass formation.
Reactions in the furnace to form glass.
Saving of heat by regeneration or recuperation.
Shaping of glass products.
Annealing of glass products.
Finishing of glass products.

To carry out these steps, modern glass factories are characterized by the use of materials-handling machinery supplying automatic and continuous manufacturing equipment, in contrast to the "shovel and wheelbarrow" methods of older factories. In spite of the modernization of plants, however, the manual charging of small furnaces is still carried on, though a dusty atmosphere is created. The trend, however, is toward mechanical batch transporting and mixing systems so completely enclosed that practically no dust is emitted at any stage of the handling of glass or raw materials.

METHODS OF MANUFACTURE

The manufacturing procedures may be divided (cf. Fig. 8.1) into four major phases: (1) melting, (2) shaping or forming, (3) annealing, and (4) finishing.

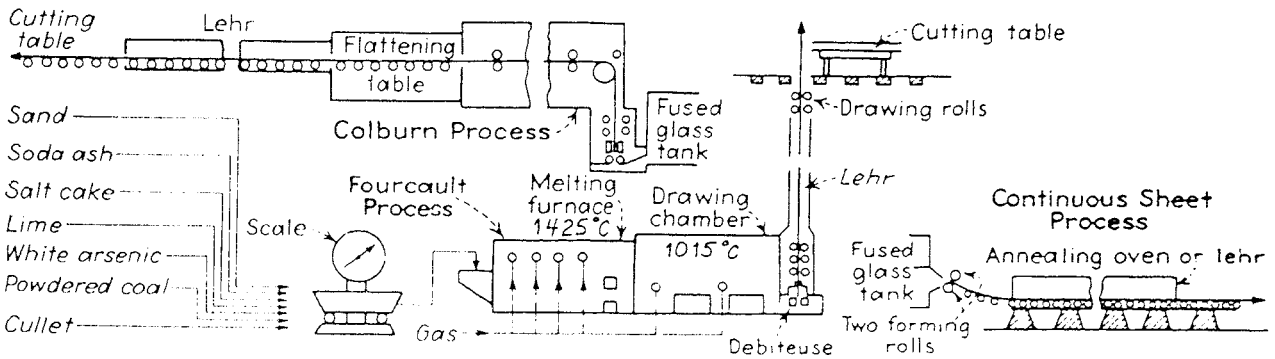
MELTING. Glass furnaces may be classified as either pot or tank furnaces (cf. Fig. 8.2, of a tank furnace). *Pot furnaces*, with an approximate capacity of 2 t or less, are used advantageously for the small production of special glasses or where it is essential to protect the melting batch from the products of combustion.[6a] They are employed principally in the manufacture of optical glass and art glass by the casting process. The pots are really crucibles made of selected clay or platinum. It is very difficult to melt glass in these vessels without contaminating the product or partly melting the container itself, except when platinum is used. In a *tank furnace*, batch materials are charged into one end of a large "tank" built of refractory blocks, some of which measure 38 x 9 x 1.5 m and have a capacity of 1350 t of molten glass. The glass forms a pool in the hearth of the furnace, across which the flames play alternately from one side and the other. The "fined"[7] glass is worked out of the opposite end of the tank, the operation being continuous. In this type of furnace, as in the pot furnace the walls gradually corrode under the action of the hot glass. The quality of the glass and the life of the tank are dependent upon the quality of the construction blocks. For this reason, much attention has been given to glass furnace refractories.[8] Small tank furnaces are called day tanks and supply a day's demand of 1 to 10 t of molten glass. They are heated either electrothermally or by gas.

The foregoing types are *regenerative* furnaces and operate in two cycles with two sets of checkerwork chambers. The flame gases, after giving up some of their heat in passing across the furnace containing the molten glass, go downward through one set of chambers stacked

[6a]t = 1000 kg.

[7]"Fining" is allowing *molten* glass sufficient time for the bubbles to rise and leave or dissolve in the glass.

[8]See Electrocast Refractories in Chap. 9.



The charge entering the furnace contains (in kilograms) approximately:

Sand	15.4	Lime	6.8
Soda ash, dense	16	Cullet	22.7
Salt cake	4.5	Other	0.5–1.0
Powdered coal	0.2		

Fig. 8.1. Flowchart for flat glass manufacture.

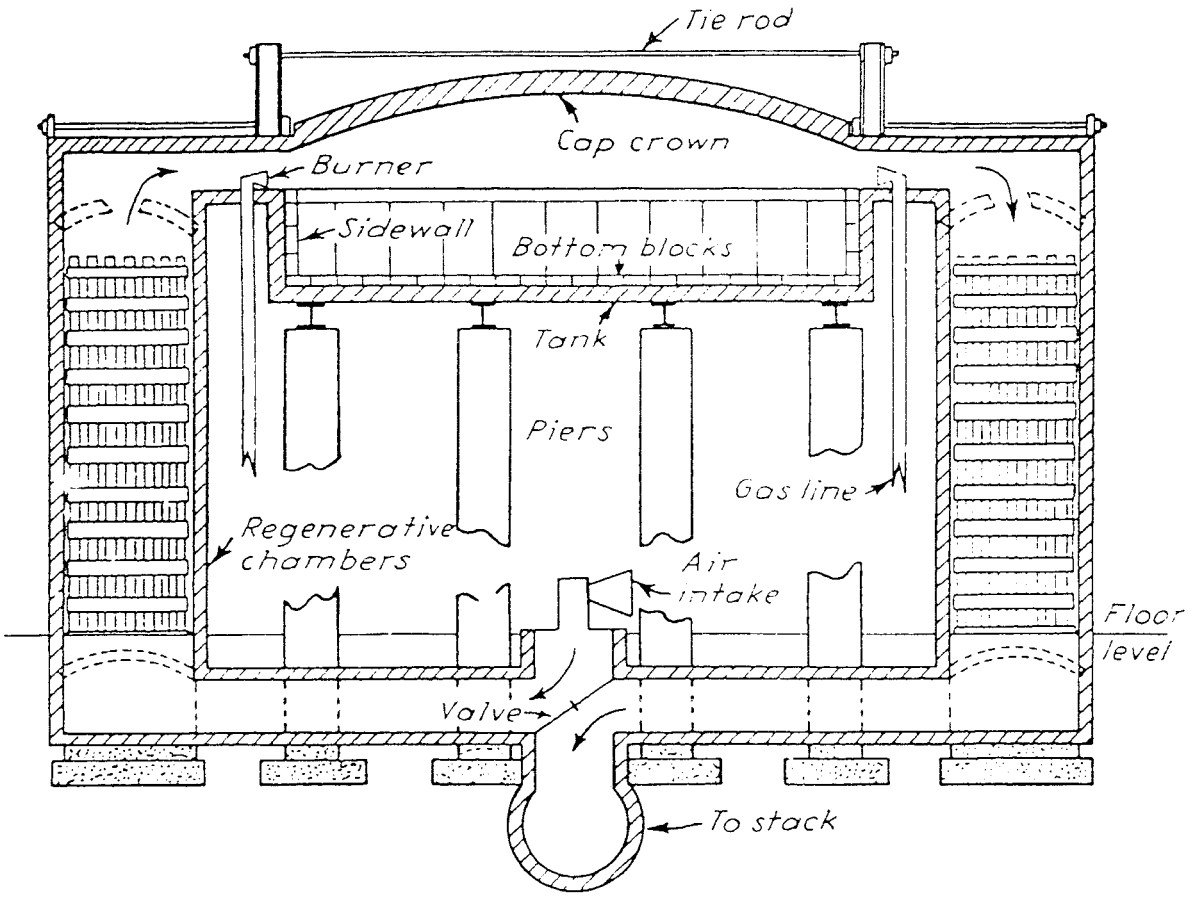


Fig. 8.2. Cross section of glass tank furnace showing regenerative chambers

with open brickwork or checkerwork. A great deal of the sensible heat content of the gases is removed thereby, the checkerwork reaching temperatures ranging from 1500°C near the furnace to 650°C on the exit side. Simultaneously, air is preheated by being passed up through the other previously heated regenerative chamber and is mixed with the burned fuel gas,[9] the resulting flame being of a higher temperature than would have been possible if the air had not been preheated. At regular intervals of 20 to 30 min, the *flow* of the air-fuel mixture, or the cycle, is reversed, and it enters the furnace from the opposite side through the previously heated checkerwork, passing through the original checkerwork, now considerably cooled. Much heat is saved by this regenerative principle, and a higher temperature is reached.

The temperature of a furnace just starting production can be raised only certain increments each day, depending upon the ability of the refractory used to stand the expansion. Once the regenerative furnace has been heated, a temperature of at least 1200°C is maintained at all times. Most of the heat is lost by radiation from the furnace, and a much smaller amount is actually expended in the melting. Unless the walls are allowed to cool somewhat by radiation, however, their temperature would become so high that the molten glass would dissolve or corrode them. To reduce the action of the molten glass, water cooling pipes are frequently placed in the furnace walls.

[9]If the fuel is producer gas, it is preheated also, but rarely if a higher energy type is employed, such as natural gas or oil.

SHAPING OR FORMING. Glass may be shaped by either machine or hand molding. The outstanding factor to be considered in *machine molding* is that the design of the glass machine should be such that the article is completed in a very few seconds. During this relatively short time the glass changes from a viscous liquid to a clear solid. It can therefore be readily appreciated that the design problems to be solved, such as flow of heat, stability of metals, and clearance of bearings, are very complicated. The success of such machines is an outstanding tribute to the glass engineer. In the following discussion the most common types of machine-shaped glass, i.e., window glass, plate glass, float glass, bottles, light bulbs, and tubing, are described.

Window Glass. For many years window glass was made by an extremely arduous hand process that involved gathering a gob of glass on the end of a blowpipe and blowing it into a cylinder. The ends of the latter were cut off, and the hollow cylinder split, heated in an oven, and flattened. This tedious manual process has now been entirely supplanted by continuous processes or their modifications, the Fourcault process and the float process, as outlined in the flowchart in Fig. 8.1.

In the *Fourcault* process a drawing chamber is filled with glass from the melting tank. The glass is drawn vertically from the kiln through a so-called "débiteuse" by means of a drawing machine. The débiteuse consists of a refractory boat with a slot in the center through which the glass flows continuously upward when the boat is partly submerged. A metal bait lowered into the glass through the slot at the same time the débiteuse is lowered starts the drawing as the glass starts flowing. The glass is continuously drawn upward in ribbon form as fast as it flows up through the slot, and its surface is chilled by adjacent water coils. The ribbon, still traveling vertically and supported by means of rollers, passes through a 7.5-m-long annealing chimney or lehr. On emerging from the lehr, it is cut into sheets of desired size and sent on for grading and cutting. This is shown in Figs. 8.1 and 8.3.

PPG Industries operates a modified Fourcault process that produces *Pennvernon* glass. Sheets of glass 3 m wide and up to 0.55 cm thick are made by varying the drawing rate from 96 cm/min for single-strength[10] to 30 cm/min for 0.55 cm. This process substitutes for the floating débiteuse a submerged draw bar for controlling and directing the sheet. After being drawn vertically a distance of 8 m, most of which is in an annealing lehr, the glass is cut. For thicknesses above single and double strength, a second annealing is given in a 36-m standard horizontal lehr.

Plate Glass. Between 1922 and 1924 the Ford Motor Co. and PPG Industries independently developed a continuous automatic process for rough-rolled glass in a continuous ribbon. The glass is melted in large continuous furnaces holding 1000 or more tons. The raw materials are fed into one end of the furnace, and the melted glass, at a temperature as high as 1595°C, passes through the refining zone and out the opposite end in an unbroken flow. From the wide refractory outlet the molten glass passes between two water-cooled forming rolls, which give it a plastic ribbon configuration. The ribbon of glass is drawn down over a series of smaller water-cooled rolls running at a slightly higher surface speed than the forming rolls. The stretching effect of the different speeds and the shrinking of the glass as it cools flatten the ribbon as it enters the annealing lehr. After annealing, the ribbon may be cut into

[10]Single-strength window glass has a thickness of 2.2 to 2.5 mm; double-strength glass measures 3 to 3.35 mm.

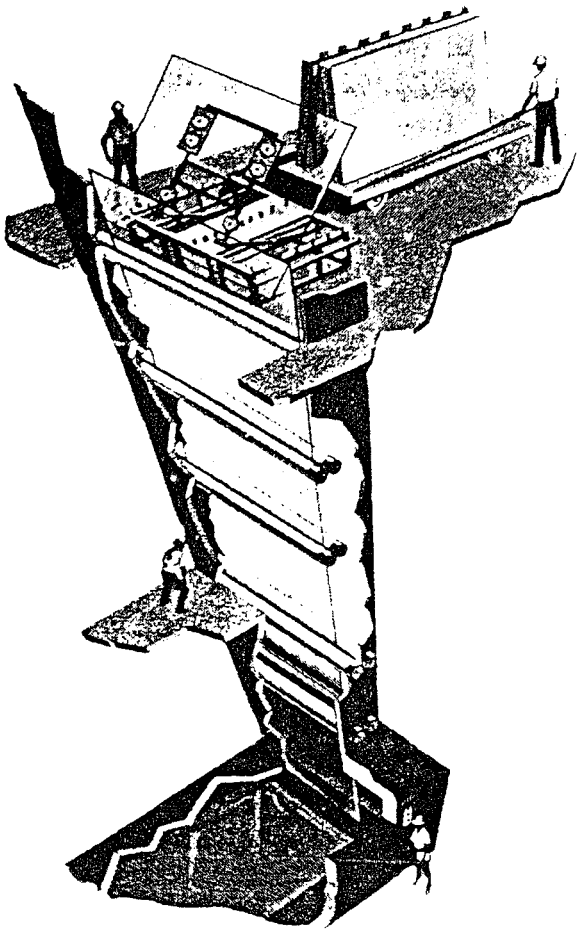


Fig. 8.3. Pictorial flowchart of modified Fourcault process for flat glass. Here the glass is continuously drawn vertically by rolls through the lehr to an automatic cutter. *(American-Saint Gobain Corp.)*

sheets for grinding and polishing, or it may progress automatically for 50 to 100 m, undergoing annealing, grinding, polishing, and inspection before it passes through cutting machines and is reduced to salable plates. Grinding and polishing removes about 0.8 mm of glass from each surface. About 30 years later this system was substantially modified by the grinding and polishing of both sides of the continuous ribbon simultaneously.

Float Glass.[11] Float glass was developed by Pilkington Brothers in England. It is a fundamental improvement in manufacturing high-quality flat glass. It has long been known that a fire-polished glass has superior reflectance and wear qualities. The float process employs the tank furnace melting system (Fig. 8.2) in which raw materials are fed into one end of the furnace and the molten glass passes through the refining zone into a narrow canal that connects the furnace with the bath (Figs. 8.4 and 8.5). Rate of flow is precisely controlled by automatically raising or lowering a gate that spans the canal. The molten glass is conducted onto and along the surface of a pool of molten tin in a nonoxidizing atmosphere under closely controlled conditions of temperature. The controlled heating melts out all irregularities and produces a glass with both sides flat and parallel.

In 1975 PPG Industries[12] made a substantial improvement in the Pilkington process by having the stream of molten glass from the melting furnace be of the desired width (usually about 4 m) as it flows onto the molten bath. This minimizes the effects of flow from a thick, unshaped mass to the sheet which introduces optical distortion.

[11]Pilkington, Flat Glass: Evolution and Revolution over 60 Years, *Glass Technol.* 17 (5) 82 (1976).

[12]ECT, 3d ed., vol. 11, 1980.

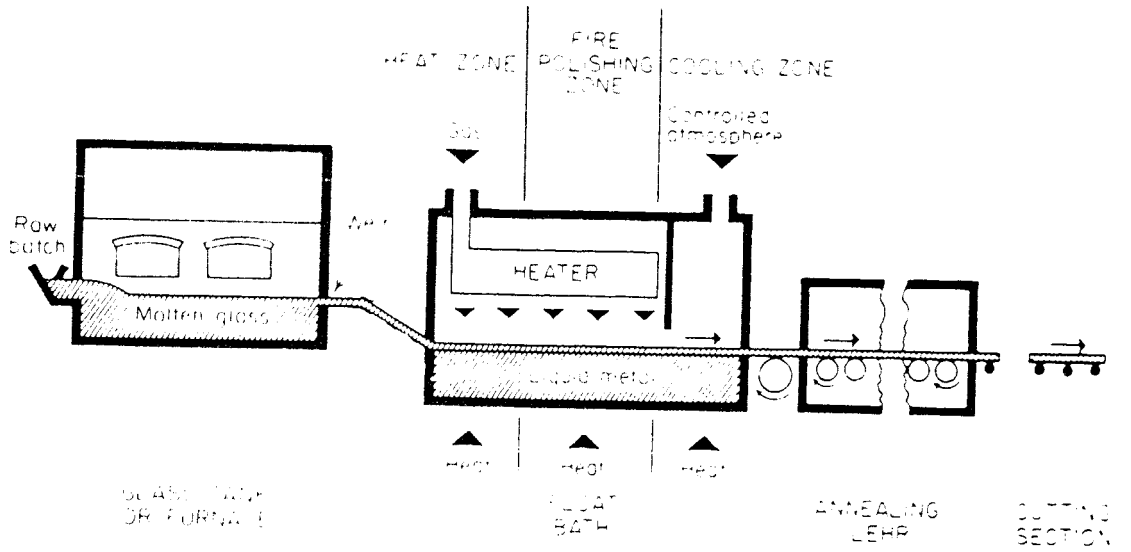


Fig. 8.4. Flowchart of a continuous process for the manufacture of float glass. (*PPG Industries.*)

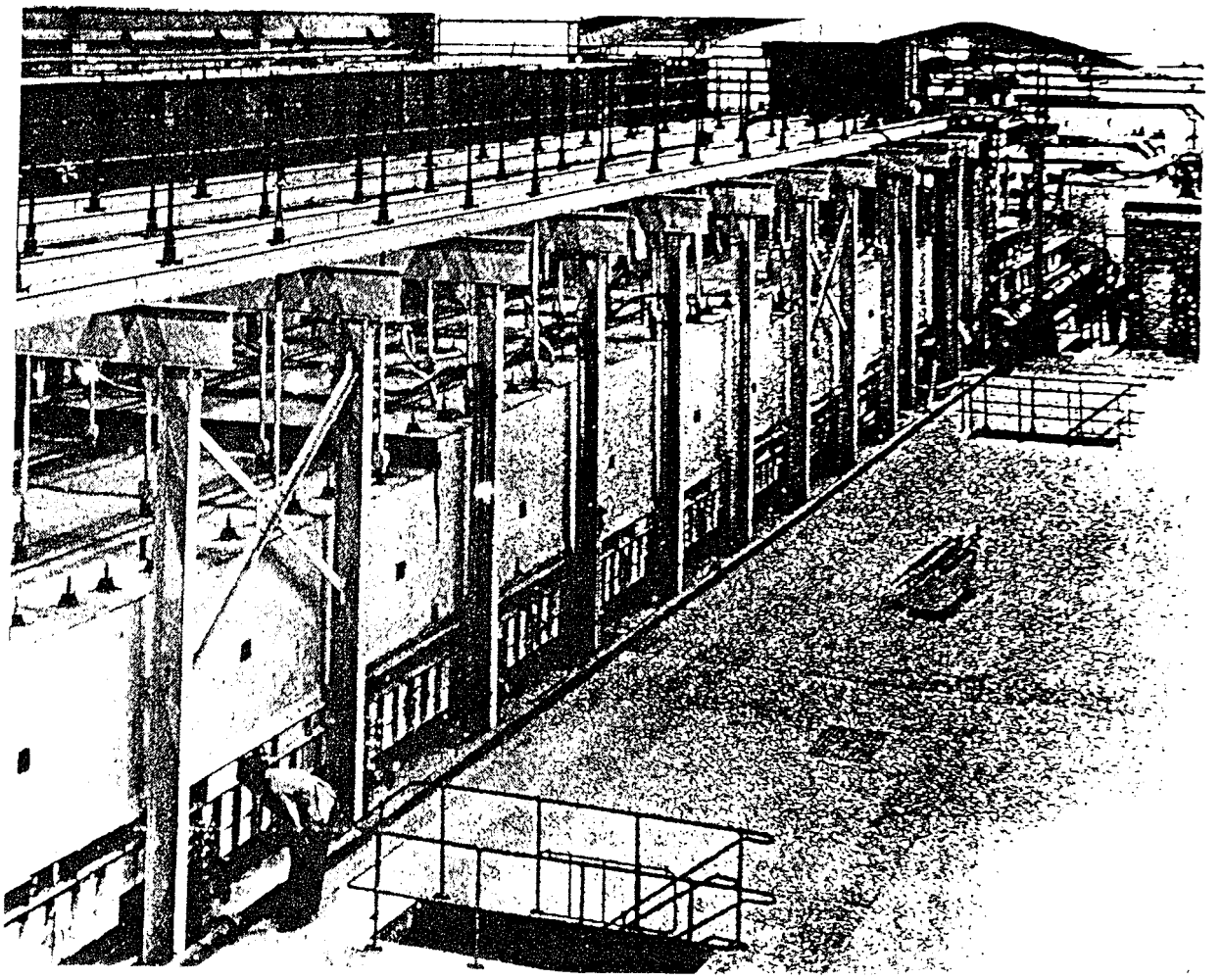


Fig. 8.5. Photograph of the Pilkington *float-bath* section in which the 2.5-m-wide glass ribbon is formed at the Pilkington Bros. float-glass process plant at St. Helens, Lancashire, England. The operating temperatures in the melting section are from about 1500 to 1200°C. [*Chem. Eng.* 71 (3) 38 (1964).] *Courtesy Pittsburgh Plate Glass Co.*)

The glass is cooled down while still on the molten metal until the surfaces are hard enough to enter the lehr without the lehr rollers spoiling the bottom surface. About 50,000 m^2 day of float can be produced in thicknesses from 3 to 19 mm and in widths of 3 to 3.5 m. This process has practically eliminated the production of ground and polished plate glass.

Wired and Patterned Glass. In patterned glass manufacture, the molten glass flows over the lip of the furnace and passes between metal rolls on which a pattern has been engraved or machined. The rolls form the glass and imprint the pattern in a single operation. Such glass diffuses the light and ensures a certain amount of privacy, which recommends it for use in rooms, doors, and shower enclosures. Such glass can be reinforced with wire during the initial forming for special safety needs, e.g., for windows near fire escapes. Both operations are pictured in Fig. 8.6.

Blown Glass. Glass blowing, one of the most ancient arts, until the last century depended solely upon human lungs for power to form and shape molten glass. Modern demands for blown glass, however, have required the development of more rapid and cheaper methods of production.[13] The machine making of bottles is only a casting operation that uses air pressure to create a hollow. Several types of machines produce *parisons*, partly formed bottles or bottle blanks. One is the suction-feed type used, with certain variations, in bulb and tumbler production. Another is the gob-feed type, which has been applied to the manufacture of all types of ware made by pressing, blowing, or a combination of "press and blow."

In the suction-feed type, glass contained in a shallow, circular revolving tank is drawn up into molds by suction. The mold then swings away from the surface of the glass, opens, and drops away, leaving the parison sustained by the neck. The bottle mold next rises into position around the parison, and a blast of compressed air causes the glass to flow into the mold. The latter remains around the bottle until another gathering operation has been performed; it then

[13]Scholes and Greene, *Modern Glass Practice*, Cahners, Boston, Mass., 1975, chap. 15.

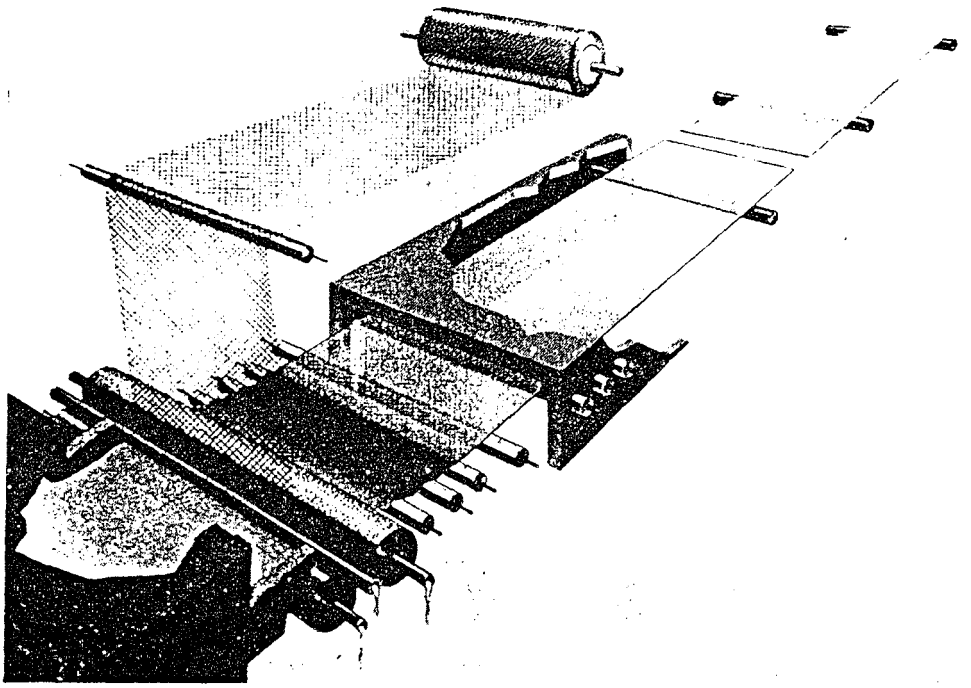


Fig. 8.6. Pictorial flowchart of a 1.5-m ribbon of wired and patterned glass. *(American Saint-Gobain Corp.)*

drops the bottle and rises to close around a fresh parison. The operations are completely automatic, and speeds of 60 units per minute are not uncommon.

The gob feeder represents one of the most important developments in automatic glass working. In this operation the molten glass flows from the furnace through a trough, at the lower end of which is an orifice. The glass drops through the orifice and is cut into a gob of the exactly desired size by mechanical shears. It is delivered through a funnel into the parison mold, which starts the formation of the bottle in an inverted position, as shown in Fig. 8.7. A neck pin rises into place, and another plunger drops from the top, whereupon compressed air in the "settle blow" forces the glass into the finished form of the neck. The mold is closed on top (bottom of the bottle), the neck pin is retracted, and air is injected in the "counter

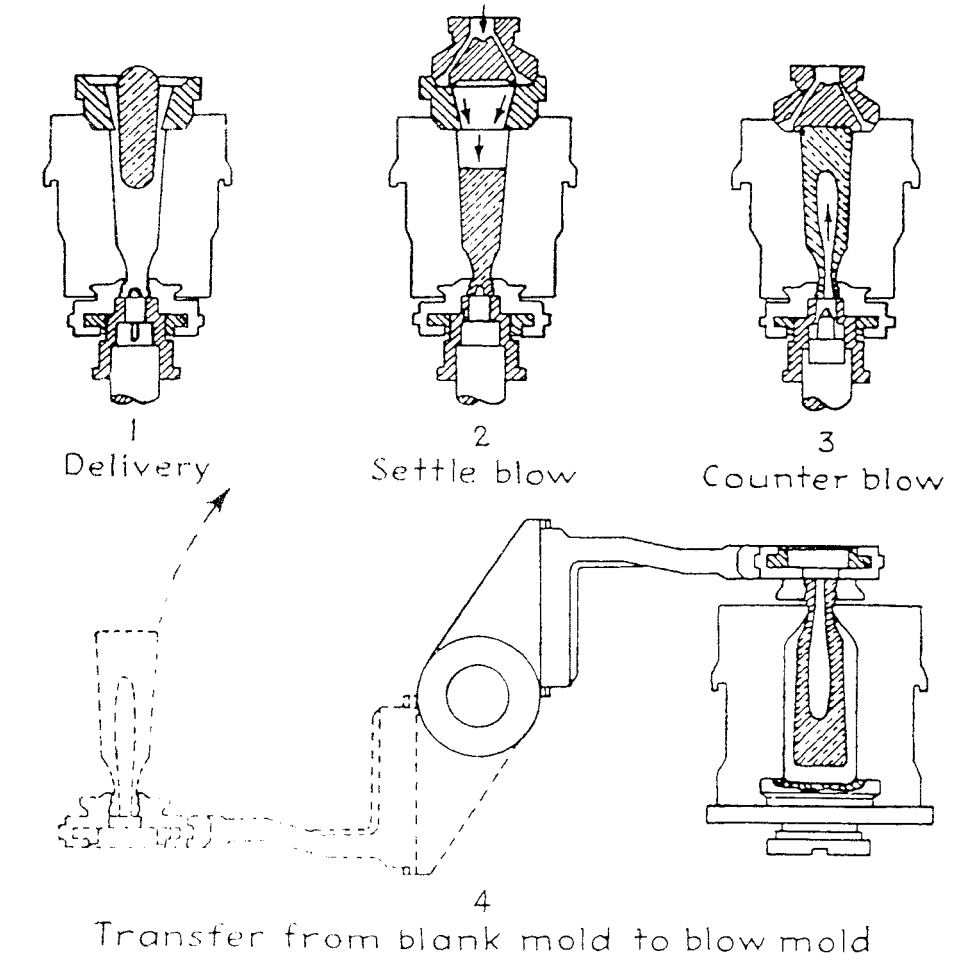


Fig. 8.7. Automatic bottle manufacture by an I-S machine. (*Glass Packer.*)

blow" through the newly formed neck to form the inner cavity. The parison mold opens, and the parison is inverted as it passes to the next station, so that the partly formed bottle is then upright. The blow mold closes around the parison, which is reheated for a brief interval. Air is then injected for the final blow, simultaneously shaping the inner and outer surfaces of the bottle. The blow mold swings away, and the bottle moves on the lehr.

Automatic bottle-blowing machines usually consist of two circular tables, known as the *parison-mold* table and the *blow* table. As the glass moves around the periphery of the table, the various operations described above take place. Table movement is controlled by compressed air which operates reciprocating pistons, and the various operations occurring on the table are coordinated with table movement by a motor-timing mechanism. This latter device constitutes one of the most vital and expensive parts of the equipment.

Light Bulbs. The blowing of a thin bulb differs from bottle manufacture in that the shape and size of the bulb are determined initially by the air blast itself and not by the mold. The molten glass flows through an annular opening in the furnace and down between two water-cooled rollers, one of which has circular depressions that cause swellings on a glass ribbon coinciding with circular holes on a horizontal chain conveyor onto which the ribbon moves next. The glass sags through these holes by its own weight. Below each hole is a rotating mold. Air nozzles drop onto the surface of the ribbon, one above each of the glass swellings or conveyor holes. As the ribbon moves along, these nozzles eject a puff of air which forms a preliminary blob in the ribbon. The spinning mold now rises, and a second puff of air, under considerably less pressure than the first, shapes the blob into the mold and forms the bulb. The mold opens, and a small hammer knocks the bulb loose from the ribbon. The bulbs drop onto a belt which carries them to the lehr rack, where they slip neck down between two parallel vertical strips which support them as they are annealed. The total time for the entire series of operations, including annealing, is about 8 min. Machine speeds as high as 2000 bulbs per minute have been attained.

Television Tubes. Television tubes are now made as large as 68 cm across and consist of three principal parts, the face phosphorescent screen, on which the picture is produced, the envelope, and the electron gun. The phosphor is applied to the face screen of the envelope either by settling or dusting. Manufacture of the glass envelope was difficult until centrifugal casting was invented, which uses a revolving mold to produce a much more uniform wall thickness. The glass parts are sealed together, using a gas flame or gas and electricity. For *colored* television tubes, the phosphor is applied to the inner surface of the screen. A perforated mask is mounted behind the screen to direct the electron beams properly. The high temperature involved in sealing cannot be employed here, since this would cause deterioration of the phosphor.

Glass Tubing. In the Danner process the molten glass flows onto the top end of a revolving, hollow clay rod inclined at about 30°. Air is blown through it and the glass on the rod slowly flows toward the bottom end where it is pulled off to form a tube. A pair of belts grip the tubing and draw it at a uniform speed. The diameter and wall thickness are controlled by the temperature, speed of drawing, and volume of air that is blown through the rod. Tubing does not require annealing.

Glass tower plates and bubble caps, prisms, and most other optical glass, most kitchenware, insulators, certain colored glasses, architectural glass, and many similar items are *hand-molded.* The process consists essentially in drawing a quantity of glass, known as the *gather,* from the pot or tank and carrying it to the mold. Here the exact quantity of glass required

is cut off with a pair of shears, and the ram of the mold driven home by hand or by hydraulic pressure. Certain glass forming is carried out by semiautomatic methods which involve a combination of the machine- and hand-molding processes previously described. Volumetric flasks and cylindrical Pyrex sections for towers are fabricated in this manner.

ANNEALING. To reduce strain, it is necessary to *anneal all glass* objects, whether they are formed by machine- or hand-molding methods. Briefly, annealing involves two operations: (1) holding a mass of glass above a certain critical temperature long enough to reduce internal strain by plastic flow to less than a predetermined maximum and (2) cooling the mass to room temperature slowly enough to hold the strain below this maximum. The lehr, or annealing oven, is nothing more than a carefully designed heated chamber in which the rate of cooling can be controlled so as to meet the foregoing requirements. The establishment of a quantitative relationship[15] between stress and birefringence caused by the stress has enabled glass technologists to design glass to meet certain conditions of mechanical and thermal stress. With the foregoing data as a basis, engineers have produced continuous-annealing equipment, with automatic temperature regulation and controlled circulation, which permits better annealing at a lower fuel cost and with less loss of product.

FINISHING. All types of annealed glass must undergo certain finishing operations which, though relatively simple, are very important. These include cleaning, grinding, polishing, cutting, sandblasting, enameling, grading, and gaging. Although all these are not required for every glass object, one or more is almost always necessary.

MANUFACTURE OF SPECIAL GLASSES

Research and development are at the heart of the new and improved types and properties of glass. This section illustrates some of the new glass products that have resulted.

FUSED SILICA GLASS. Fused silica glass, or vitreous silica, may be made by fusing pure silica, but such products are usually blebby and difficult to produce in transparent form. It is now manufactured by Corning[16] by vapor-phase high-temperature pyrolysis of silicon tetrachloride. This type of process lends itself naturally to controls which permit chemically pure SiO_2. The raw silica produced in this manner is in the form of plates, or boules. The high temperature of the reaction tends to drive off undesired contaminants, giving fused-silica impurities in the order of 1 part in 100 million. This fused-silica glass has remarkable properties (Table 8.3) and has the lowest ultrasonic absorption of any material. Because of its low thermal expansion it is used for telescope mirrors, e.g., in a 158-cm mirror for a telescope at the U.S. Naval Observatory.

HIGH-SILICA GLASS. This product, known as Vycor,[17] constitutes an important advance toward the production of a glass approaching fused silica in composition and properties. This has been accomplished with the avoidance of former limitations on melting and forming.

[15]Shand, op. cit., pp. 103–109.

[16]ECT, 3d ed., vol. 11, 1980, pp. 807–880.

[17]Corning Glass Works, U.S. Patent 2,106,744 (1938), and 2,221,709 (1940).

The finished articles contain approximately 96% silica and 3% boric oxide, and the rest is alumina and alkali. Borosilicate-glass compositions of about 75% silica content are used in the earlier stages of the process, in which the glasses are melted and molded. After cooling, the articles are subjected to heat treatment and annealing, which induce the glass to separate into two distinct physical phases. One of these phases is so high in boric and alkaline oxides that it is readily soluble in hot acid solutions, whereas the other is rich in silica and therefore insoluble in these solutions. The glass article is immersed in a 10% hydrochloric acid (98°C) bath for sufficient time to permit the soluble phase to be virtually all leached out. It is washed thoroughly to remove traces of the soluble phase, as well as impurities, and subjected to another heat treatment that serves to dehydrate the body and to convert the cellular structure to a nonporous vitreous glass. In the course of these processes the glassware undergoes a shrinkage in linear dimensions amounting to 14 percent of its original size. Table 8.3 compares its properties with those of other glasses. This method of glass manufacture furnishes a product that can be heated to a cherry red and then plunged into ice water without any ill effects. Also, this glass has high chemical durability and is extremely stable to all acids except hydrofluoric, which, however, attacks this glass considerably more slowly than others. Its shrinkage is also proportionately even, so that the original shape is preserved.

COLORED AND COATED GLASSES. Although for many centuries they were used merely for decoration, today transparent colored glasses are essential for both technical and scientific purposes and are produced in many hundreds of colors. Colored glass may be one of three types: (a) Color is produced by the absorption of certain light frequencies by agents in solution in the glass. The coloring agents of this group are the oxides of the transition elements, especially the first group, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu. This class can be subdivided into those in which the color is due to the chemical structural environment and those in which the color is caused by differences in state of oxidation. As an example of the former, NiO dissolved in sodium-lead glass yields a brown color, but in a potash glass it produces heliotrope. In the latter, chromium oxides produce colors ranging from green to orange, depending on the proportion of the basic oxide Cr_2O_3 to the acidic oxide and the composition of the glass, i.e., whether it is basic or acidic. (b) Color is produced by colloidal particles precipitated within an originally colorless glass by heat treatment. The classic example is the precipitation of colloidal gold, producing gold-ruby glass. (c) Color is produced by microscopic or larger particles which may be colored themselves, such as selenium reds (SeO_2) used in traffic lights, lantern globes, etc., or the particles may be colorless, producing opalescent glass.

Coated glasses are made by depositing transparent metallic films on the surface of clear or colored glass. The films are designed to provide specific transmission and reflection characteristics, which are important to the architect today.

Opal, or translucent, glasses are clear when molten but become opalescent as the glass is

***Table* 8.3** Comparative Properties of Glasses

	Common Lime	Pyrex Borosilicate	Vycor 96% Silica	Fused Silica	Pyroceram
Softening point °C	715	746	1530	1525	1250
Annealing point °C	527	450	1020	1085	
Specific gravity	2.50	2.23	2.18	2.20	2.60
Young's modulus GPa	70		68		

SOURCE: ECT, 3d ed., vol. 11, 1980, p. 830

worked into form, because of the separation and suspension of minute particles of various type, size, and density in the medium, which disperse the light passing through.

Opal glass is often produced by growing nonmetallic crystals from nucleated silver particles developed from an original clear glass containing silver. It is employed for architectural effects, e.g., in window louvers, for transmission of specified wavelengths, and for tableware.

SAFETY GLASS. Safety glasses[18] may be grouped into two general classes: laminated safety glass and heat-strengthened (or tempered) or case-hardened safety glass. Wired glass may also be considered safety glass (Fig. 8 .6).

Laminated safety glass, which is the most widely used in this country, consists of two sheets of thin plate glass, each of which is about 3 mm thick, with a sheet of nonbrittle plastic material between. The plastic and glass are washed, and an adhesive is applied to the glass (if the plastic used requires it, such not always being the case). The glass and plastic sheet are pressed together under moderate heat to seal the edges. The glass is subjected to moderate temperatures and hydraulic pressures in an autoclave, in order to bring the entire interlayer into intimate contact, after which the edges of the sandwich may be sealed with a water-resistant compound.

The glass used in the manufacture of laminated safety glass has the same physical properties as ordinary glass, so that the safety features depend solely upon the ability of the plastic interlayer to hold fragments caused by accidental breaking of the glass itself. The first plastic used commercially was cellulose nitrate, which was replaced by cellulose acetate. Now practically all laminated safety glass uses polyvinyl butyral resin. This vinyl plastic is more elastic than cellulose acetate, since it stretches under relatively low stresses up to its elastic limit, after which considerable additional stress is necessary to make it fail. It remains clear and colorless under all conditions of use, is not affected by sunlight, and does not need adhesives or water-resistant compounds in manufacturing.

Tempered, or strengthened,[19] *glass* is very strong and tough. It is used for doors and windows of automobiles and for pipe. It possesses high internal stresses and, if the surface is broken, shatters into many pieces. Its manufacture involves controlled heat annealing whereby the nonuniform stresses in glass are replaced by controlled, uniform, low-level stresses. Such glass is really very strong in compression and very weak in tension. *Physical tempering* is an outgrowth of the study of annealing and is less drastic than the quenching process long used for making Prince Rupert drops. The already-formed glass vessel or sheet to be strengthened by tempering or annealing is heated to some temperature, e.g., 425°C. just below its softening point, and then quenched in air, molten salt, or oil. During this tempering, a sandwich effect results when the exterior, or skin, of the glass cools rapidly and becomes hard and the interior cools more slowly and continuously and contracts after the exterior has become rigid. Thus the interior pulls on the *outside* surface, *compressing* it, whereas the *interior* develops compensating *tension* and provides a threefold increase in strength. Chemcor[20] is *chemically strengthened* glass that may have three to five times the strength of even physically tempered products. It duplicates the stresses just described by physical means (controlled quenching). This has been done by ion exchange with the outer

[18]Randolph, Evolution of Safety Glass, *Mod. Plast.* **18** (10) 31 (1941); cf. Weidlein, History and Development of Laminated Safety Glass, *Ind. Eng. Chem.* 31 563 (1939).

[19]Olcott, Corning Glass Co., Chemical Strengthening of Glass, *Science* **140** 1189 (1963).

[20]Corning Chemical Engineering Achievement, *Chem. Eng.* **70** (23) 233 (1963); **71** (1) 36 (1964).

layer of glass by immersing sodium glass in a molten-lithium salt bath, resulting in a lithium glass on the surface and a sodium glass in the interior. This alkali substitution results in a product with the surface under compression, since the lithium glass has a lower coefficient of expansion and hence shrinks less on cooling than the interior sodium glass. Such tempered glass can be bent and twisted. It does not fracture as easily as ordinary glass, and tests indicate that tableware sold as Centura, manufactured by chemical tempering, is lighter in weight and three times stronger than ordinary tableware.

FOTOFORM. Fotoform glass is a photosensitive glass that is essentially a lithium silicate modified by potassium oxide and aluminum oxide and contains traces of cerium and silver compounds as photosensitive ingredients. Under exposure to ultraviolet light, nuclei are formed by silver sensitized by the cerium, around which an image of lithium metasilicate results upon development by heat treatment to near 600°C. The acid-soluble lithium metasilicate can be removed by 10% hydrofluoric acid. If light exposure is made through a negative (photographically made from a drawing), the final result is a glass reproduction with great accuracy and intricate detail. For example, sheet-glass electrical-circuit boards can be made cheaply and accurately. The process has been termed *chemical machining* of glass.

PHOTOCHROMIC SILICATE GLASSES.[21] Photochromic silicate glasses supplement the just presented Fotoform glass but possess the following unusual properties: *optical darkening* in light from ultraviolet through the visible spectrum; *optical bleaching*, or fading in the dark; and *thermal bleaching* at higher temperatures. These photochromic properties are truly *reversible* and not subject to *fatigue*. Indeed, specimens of this photochromic glass have been exposed to thousands of cycles without any deterioration in performance. The scientific explanation of this photochromic process is the manufacture of a glass in which submicroscopic silver halide particles exist, which react differently from ordinary photographic silver halides when exposed to light. Such tiny particles are about 5 nm in diameter and have a concentration of about 10^{15} per cubic centimeter, and are embedded in rigid, impervious, and chemically inert glass, which ensures that the photolytic "color centers" cannot diffuse away and grow into stable, larger silver particles or react chemically to produce an irreversible decomposition of the silver halide, such as takes place in the photographic process when larger, opaque silver particles are formed. These two processes may be diagramed as follows:

IRREVERSIBLE PHOTOGRAPHIC PROCESS

$$n\mathrm{AgCl} \xrightarrow{\text{light}} n\mathrm{Ag}^0 + n\mathrm{Cl}^0$$

$$\searrow$$

$n(\mathrm{Ag}^0)$ latent image silver particle

REVERSIBLE PHOTOCHROMIC PROCESS

$$\mathrm{AgCl} \underset{\text{light 2 or heat}}{\overset{\text{light 1}}{\rightleftharpoons}} \mathrm{Ag}^0 + \mathrm{Cl}^0 \text{ or } \begin{matrix}\text{light 1 outdoors, day} \\ \text{light 2 outdoors, night}\end{matrix}$$

$$\mathrm{Ag}^+ + \mathrm{Cu}^+ \underset{\text{light or heat}}{\overset{\text{light}}{\rightleftharpoons}} \mathrm{Ag}^0 + \mathrm{Cu}^{2+}$$

[21] Armestead and Stookey, Photochromic Silicate Glass Is Sensitized by Silver Halides, *Science* **144** 150 (1964).

The primary photolytic reaction is the freeing of an electron from Cl^- to be caught by an Ag^+ ion, resulting in $Ag^0 + Cl^0$. The applications of these photochromic glasses are in sunglasses, windows, and instruments, and processes wherein dynamic control of sunlight is desired.

GLASS-CERAMIC.[22] Glass-ceramic is a material melted and formed as glass, and then converted largely to a crystalline ceramic by processes of *controlled devitrification*. Ceramics are usually bodies with crystalline and high-melting particles bound together either in a vitreous matrix or by fusion of the particles at their grain boundaries. The vitreous matrix results from chemical reactions between small amounts of fluxes included in the raw materials and the crystalline constituents. These glass ceramics, after first being machine-fabricated in the glassy state, are followed by catalytic nucleation around a minor but important ingredient such as TiO_2 through heat treatment. This is accomplished by heating the glass 30 to 100°C above the annealing point and maintaining it at this temperature for one hour or more. Crystals are then grown on the nuclei by heating the glass to 750 to 1100°C, which is within the devitrifying range of the particular composition involved. Such crystals are much smaller and more uniform than those in conventional ceramics. Properties of ceramics produced from glass correspond more closely to those of ceramics than to those of unconverted glass. The glass-ceramic possesses superior rigidity and other desirable mechanical and thermal properties. The bodies are usually opaque, glossy, either white or colored, and nonporous; some compositions have outstanding electrical properties. Nonporous, fine-grained, crystalline microstructure glass-ceramics have higher flexural strength than conventional ceramics of similar chemical composition, ranging up to 200 MPa and above. They are more refractory than common glasses but less refractory than common oxide refractories. They can withstand temperatures of 1000 to 1100°C for more than 1000 h without sustaining any appreciable changes in properties. The low-thermal expansion formulations are practically immune to breakage by thermal shock. These products can be fabricated with close dimensional tolerances into a wide variety of shapes and sizes, employing conventional glass-forming methods. They are used for radomes, for guided missiles, in various electronic devices, and, under the Corning trademark Pyroceram, in cook-serve-freeze utensils.

FIBERGLASS. Fiberglass (cf. Chap. 35, Synthetic Fibers), although not a new product, owes its enhanced usefulness to its extreme fineness (often about 10 μm, but it may be down to 5 μm or less). It can be drawn into thread or blown into a mat for insulation, tape, and air filters. The drawn fibers are used to reinforce various plastics and the composite product is fabricated into pipes, tanks, and sporting goods, such as fishing rods and skis. The most common resins used are epoxies and polyesters.

A special glass, low in silica, is used for the production of fibers (Table 8.2, no. 16). Efforts have been made to produce a fiber for the reinforcement of concrete that would not be attacked and weakened by alkali. The most successful of these alkali-resistant fibers are made from glass containing up to 17% ZrO_2. This additive makes the glass very expensive, and it is also difficult to produce fibers from it. Fibers produced from a slate-limestone glass are claimed to be easier to produce than zirconia-glass fibers and to possess better alkali resistance.[23]

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[22]ECT, 3d ed., vol. 11, 1980, pp. 891–892; Stookey, Glass Chemistry as I Saw It, *CHEMTECH* **1** (8) 458 (1971).

[23]Alkali Resistance of Slate-Limestone Fibers Probed, *Chem. Eng. News* **61** (3) 47 (1983).

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Chapter 9

Salt and Miscellaneous Sodium Compounds

Many sodium salts are of definite industrial necessity. Most of them are derived directly or indirectly from ordinary salt so far as their sodium content is concerned. In one sense, the sodium may be viewed simply as a carrier for the more active anion to which the compound owes its industrial importance. For instance, in sodium sulfide, it is the sulfide part that is the more important. Similarly, this is the case with sodium thiosulfate and sodium silicate. The corresponding potassium salt could be used in most cases; however, sodium salts can be manufactured more cheaply and in sufficient purity to meet industrial demands. In addition to the sodium salts discussed in this chapter, sodium salts are described elsewhere: sodium chlorate and perchlorate in Chap. 14; sodium hypochlorite in Chap. 13, which includes various sodium alkali compounds; sodium phosphates in Chap. 16; sodium nitrate in Chap. 15; and sodium bichromate and sodium borate in Chap. 20.

The U.S. production of sodium salts is presented in Table 9.1

SODIUM CHLORIDE, OR COMMON SALT

HISTORICAL. The salt industry is as old as humankind. Salt has long been an essential part of the human diet. It has served as an object of worship and as a medium of exchange, lumps of salt being used in Tibet and Mongolia for money. Its distribution was employed as a political weapon by ancient governments, and in Oriental countries high taxes were placed on salt. Salt is a vital basic commodity for life but is also a source of many of the chemicals that are now the mainstay of our complex industrial civilization. The word "salary" is derived from the word "salt."

USES AND ECONOMICS. Sodium chloride is the basic raw material of a great many chemical compounds, such as sodium hydroxide, sodium sulfate, hydrochloric acid, sodium phosphates, and sodium chlorate and chlorite, and it is the source of many other compounds through its derivatives.[1] Practically all the chlorine produced in the world is manufactured by the electrolysis of sodium chloride. Salt is used in the regeneration of sodium zeolite water softeners and has many applications in the manufacture of organic chemicals.

The production of chlorine and sodium hydroxide accounts for 50 percent of salt usage in

[1]Saltmakers Scent New Success, *Chem. Week* 105 (21) 59 (1969).

***Table* 9.1** U.S. Production of Sodium Salts (thousands of metric tons)

	1962	1968	1972	1980
Sodium chloride	17,550	36,360	40,520	37,335
Sodium sulfate, anhydrous	187	652	720	467
Glauber's salt and crude salt cake	756	681	473	665
Sodium sulfite	39	216	200	135
Sodium hydrosulfide	18	32	27	18
Sodium hydrosulfite	23	36	42	50
Sodium silicate	467	570	597	666

SOURCES: *Chemical Marketing Reporter; Current Industrial Reports* Dept of Commerce.

the United States. Soda ash manufacturing requires 6 percent; however, this will decline in the coming years as natural soda ash from Trona increases in production and more old ammonia–soda ash plants are closed down, primarily because they pollute streams. Highway use accounts for 21 percent, and salt for food uses and related activities is about 3 percent. All other chemical requirements come to about 20 percent of the total use.

The world production of salt in 1980 was over 163×10^6 t.[1a] U.S. production was 37×10^6 t and imports amounted to 4.8×10^6 t, with a combined value of over $700 million. Reserves are large in the principal salt-producing countries, but the grade is unknown.[2] The oceans offer an additional almost inexhaustible supply of salt.[3] Current prices can be found in a number of publications including *Chemical Marketing Reporter.*

MANUFACTURE. Salt occurs throughout the United States. In 1980, Louisiana was the largest salt-producing state with 31 percent of the total output; Texas was second, with 24 percent. New York produced 14 percent, Ohio 7 percent, Michigan 6 percent, Kansas 4 percent, and West Virginia 2 percent.[4]

Salt is obtained in three different ways, namely, solar evaporation of seawater on the Pacific coast or from western salt-lake brines, from mining of rock salt, and from well brines.[5] The purity of the salt obtained from the evaporation of salt water is usually over 99%. Mined salt varies very widely in composition, depending upon the locality but is normally above 95%. Some rock salt, however, runs as high as 99.5% pure. The solution obtained from wells is usually about 98% pure and depends to a great extent on the purity of the water forced down into the well to dissolve the salt from the rock bed. For many purposes, the salt obtained from mines and by direct evaporation of salt solutions is pure enough for use; however, a portion must be purified to remove such materials as calcium and magnesium chlorides.

Solar evaporation is used extensively in dry climates, where the rate of evaporation depends on the humidity of the air, wind velocity, and amount of solar energy absorbed. San Francisco, southern California, and the Great Salt Lake area are the primary producing areas in the United States. Solar evaporation represents only a small part of the total U.S. production but a large part of the world production.

[1a]t = 1000 kg.

[2]Lefond, *Handbook of World Salt Resources*, Plenum, New York, 1969.

[3]*Statistical Abstracts of the United States*, Dept. of Commerce, Bureau of the Census (yearly).

[4]*Minerals Yearbook 1980*, Dept. of the Interior, Bureau of Mines, vol. 1, 1981.

The mining of rock salt uses methods similar to coal mining. As the salt is removed, large rooms are formed, supported by pillars of salt.

Salt brine is obtained by pumping water into a salt deposit and bringing the brine to the surface. Two concentric pipes are used with water being forced down the center pipe and brine returning to the surface through the annular space between the two pipes. However, newer wells are often drilled to the base of the salt cavity, water is injected under pressure into one well, and the brine is removed from a nearby well by exerting sufficient pressure on the first well to make a connection between the two wells. This is known as hydraulic fracturing and has reduced the time required to achieve maximum production.

The vacuum pan system, as shown in Fig. 9.1, employing multiple-effect evaporators, is the most common method of producing salt from brine. The type of evaporator may vary, but modern units are generally forced-circulation units constructed of Monel.[6]

SODIUM SULFATE (SALT CAKE AND GLAUBER'S SALT)

The production of salt cake, or crude sodium sulfate, is nearly equally divided between that from natural sources and that from by-product output from rayon, lithium, hydrochloric acid, and chrome chemicals manufacture. The brines of Searles Lake at Trona, Calif., subterranean brines in Seagraves and Brownfield, Tex., and the Great Salt Lake in Utah account for the U.S. natural production. A large quantity is also imported, mainly from Canada. In 1980, natural salt-cake producers supplied 525,000 t, by-product sources supplied 607,000 t, and imports amounted to 225,000 t. However, the United States also exported 375,000 t.[7] The wholesale price was $55 per metric ton.

USES AND ECONOMICS. About 50 percent of the sodium sulfate consumed in this country is used in the manufacture of kraft pulp. Salt cake, after reduction to sodium sulfide or hydrolysis to caustic, functions as an aid in digesting pulpwood and dissolves the lignin. About 38 percent goes into the compounding of household detergents, and the remainder into a variety of uses such as glass, stock feeds, dyes, textiles, and medicine.

MANUFACTURE. Natural brines account for 46 percent of the sodium sulfate production from three producers (Fig. 9.2). The most important by-product source recently has been chrome chemicals manufacture (Chap. 20).

[6]Evaporation Process Solves Vacuum-Related Problems, *Chem. Eng.* 81 (19) 72 (1974).

[7]Sulfates Are Won from Salt Lake, *Chem. Eng.* 78 (1) 46 (1971); Slow Sales Don't Faze Salt-cake Makers, *Chem. Week* 129 (25) 24 (1981).

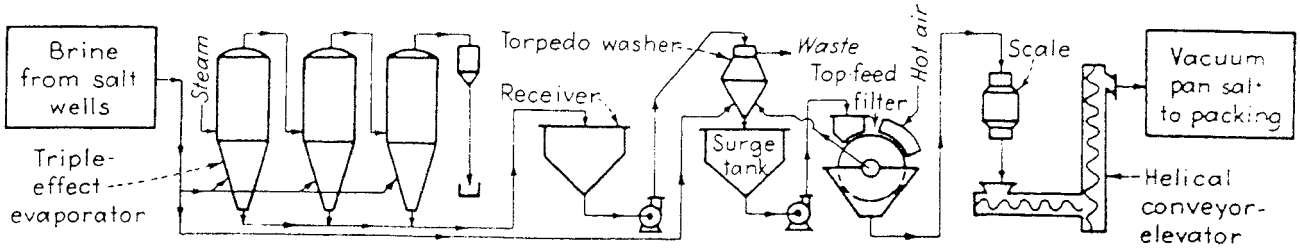


Fig. 9.1. Vacuum pan system for producing salt from brine.

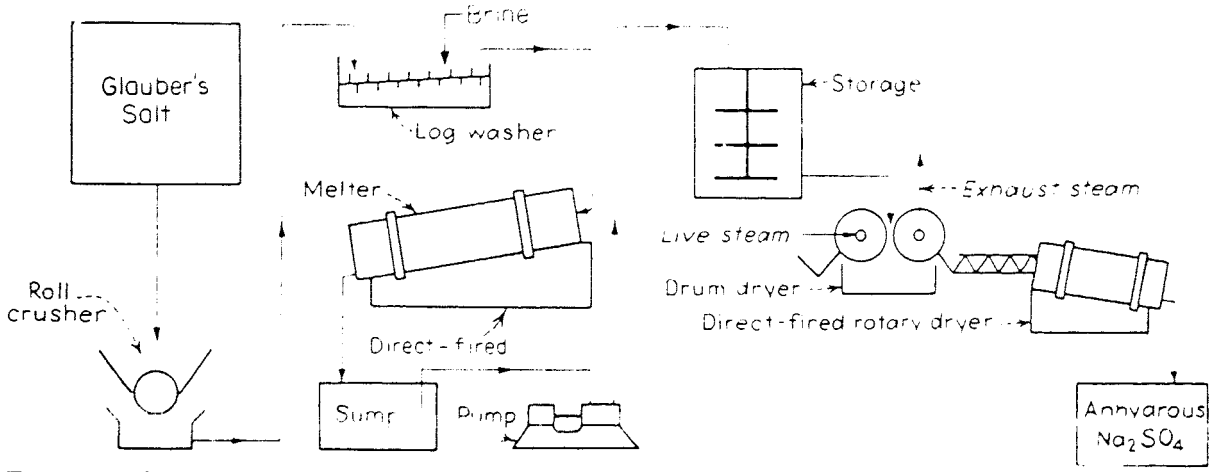


Fig. 9.2. Flowchart for production of naturally occurring sodium sulfate by the three-stage procedure NOTE: Seventy-one percent of the dehydration is accomplished in the drum driers, while 29 percent is done in the direct-heat driers

The equations for the production of salt cake from sulfuric acid and salt by the Mannheim process are:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl$$

The procedure for commercializing these reactions is described under Hydrochloric Acid in Chap. 20. When the temperature has reached the proper level in the furnace, the finely ground salt and other raw materials are charged. The furnace runs continuously, batch after batch, until it is shut down for periodical cleaning and repair. Most products from the Mannheim furnace go into the manufacture of other materials in the same plant where the furnace is operated.

Another method of making high-grade sodium sulfate, which originated in Europe, is the Hargreaves process. The equation for the reaction is

$$4NaCl + 2SO_2 + 2H_2O + O_2 \rightarrow 2Na_2SO_4 + 4HCl$$

Three plants use the Mannheim and Hargreaves processes.

MANUFACTURE OF GLAUBER'S SALT. Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) is made by dissolving salt cake in mother liquor, removing the impurities, clarifying, and crystallizing. The solution is then treated with a paste of chloride of lime, followed by milk of lime in sufficient quantities to neutralize the solution. The precipitated impurities of iron, magnesium, and calcium are allowed to settle, and the clear solution is run to crystallizers by side outlets. The precipitated mud is washed with water, and the water is used as makeup for the process. When the solution cools to room temperature, the pan is drained and the crystals are collected and centrifuged.

Pure anhydrous sodium sulfate is increasingly in demand by the kraft paper industry. It is made by dehydrating Glauber's salt in a brick-lined rotary furnace, by crystallizing out from a hot, concentrated solution, or by chilling and dehydrating. Figure 9.2 shows the steps in the production of anhydrous sodium sulfate from naturally occurring Glauber's salt.

SODIUM BISULFATE, OR NITER CAKE

Sodium bisulfate is commonly called *niter cake* because it was formerly obtained by the obsolete process of reacting sodium nitrate, or niter, with sulfuric acid:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

It may also be formed when salt is moderately heated with sulfuric acid:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

It is an easily handled dry material that reacts like sulfuric acid. Major uses are in the manufacture of acid-type toilet bowl cleaners and for industrial cleaning and metal pickling. Minor uses are in dye baths, carbonizing wool, and various chemical processes.

SODIUM BISULFITE

USES AND ECONOMICS. Sodium bisulfite finds industrial use either in solution or as a solid. The solid is of the anhydrous form, and the pure reagent has the formula $NaHSO_3$. The commercial product consists almost entirely of $Na_2S_2O_5$ (sodium pyrosulfite), or sodium metabisulfite, which is the dehydrated derivative of two molecules of sodium bisulfite. The solutions may be easily shipped, stored, and handled in 316 stainless steel. Kynar and polyvinyl chloride (PVC) are also suitable construction materials with appropriate temperature limitations. This compound is usually sold as either a 38 or a 43% solution.

Major uses are as chemical intermediates, in pharmaceuticals, and in food preservatives. Minor uses are as an antichlor for pulp, paper, and textiles, and in water treatment and pollution control. It is also used in the tanning industry as a reducing agent for chrome solutions and in the manufacture of photographic and organic chemicals. In the textile field it is a bleaching agent and is a raw material for the manufacture of hydrosulfite solutions.

MANUFACTURE. Sodium bisulfite is produced by passing 7 to 8% sulfur dioxide through mother liquors from previous processes containing in solution small amounts of sodium bisulfite and in suspension a considerable amount of soda ash. The reaction taking place is:

$$2NaHSO_3 + \underline{2Na_2CO_3} + 2H_2O + 4SO_2 \rightarrow \underline{6NaHSO_3} + 2CO_2$$

The product is obtained as a suspension, which is removed from the solution by centrifugation.

SODIUM SULFITE

USES AND ECONOMICS. Sodium sulfite is a compound that is very easily oxidized. For this reason, it is employed in many cases where a gentle reducing agent is desired, e.g., to bleach wool and silk, as an antichlor after the bleaching of yarns, textiles, and paper, as a preservative for foodstuffs, and to prevent raw sugar solutions from coloring upon evaporation. It is very

widely used in the preparation of photographic developers to prevent the oxidation of hydroquinone and other agents. It has a small application in the field of medicine as an antiseptic and as an antizymotic for internal use. About 60 percent of the total merchant market is in the paper industry. While merchant capacity is about 145,000 t/year, the paper mills have twice this capacity for captive use. The demand for boiler feedwater treatment is about 15 percent and for photography 12 percent. It is used to remove oxygen from water and thus helps to prevent corrosion and scale formation. There were four major producers in 1981, one of which provided 50 percent of the product.

MANUFACTURE. The most important commercial procedure for preparing this compound involves passing sulfur dioxide into a solution of soda ash until the product has an acid reaction. At this point the solution consists chiefly of sodium bisulfite. This may be converted into sodium sulfite by adding more soda ash to the solution and boiling until all the carbon dioxide has evolved. After the solution has settled, it is concentrated, and crystals of $Na_2SO_3 \cdot 7H_2O$ settle out upon cooling.

SODIUM HYDROSULFITE

USES AND ECONOMICS. One of the most important chemicals in the dyeing and printing industries is sodium hydrosulfite. It is a very powerful reducing agent and has a specific action on many dyes, particularly vat dyes, reducing them to the soluble form. This reducing agent is employed for stripping certain dyes from fabrics and for bleaching straws and soaps. Formerly, one of the main difficulties with this compound was a lack of stability; however, this has been corrected, and it may be shipped and stored. Dye-house workers call it simply "hydro."

The pulp and paper industry is starting to switch from zinc to sodium hydrosulfite bleaching to meet EPA regulations for zinc discharge from their plants. The demand in the clay industry, where "hydro" is used to remove the red iron color from clay used in manufacturing coated papers and china is expected to grow. It is widely used in the dyeing of denim with indigo. If the popularity of blue denim declines the sodium hydrosulfite business would suffer. In 1981 there were two producers with six plants, and the demand was 50,000 t.

MANUFACTURE. There are two methods of manufacture, which require zinc dust. In the first process the zinc dust is allowed to reduce sodium bisulfite at room temperature:

$$2NaHSO_3 + H_2SO_3 + Zn \rightarrow ZnSO_3 + Na_2S_2O_4 + 2H_2O$$

The products of the reaction are treated with milk of lime to neutralize any free acid, and this reduces the solubility of the $ZnSO_3$, which is filtered off. Sodium chloride is added to salt out the $Na_2S_2O_4 \cdot 2H_2O$, which is dehydrated with alcohol and dried. The crystals are stable only in the dry state. The second process consists of treating an aqueous suspension of zinc dust in formaldehyde with sulfur dioxide at 80°C. A double-decomposition reaction is then carried out with soda ash to form the sodium salt. A pure product is obtained by evaporation under vacuum. Another method is to reduce sodium sulfite solution with sodium amalgam [formed in the production of chlorine using a mercury cell (Chap. 10) at a controlled pH in the range 5 to 7].

Sodium hydrosulfite can also be produced from sodium formate formed as a by-product in

the manufacture of pentaerythritol. The sodium formate in an alkaline alcoholic solution is reacted with sulfur dioxide:

$$HCOONa + 2SO_2 + NaOH \rightarrow Na_2S_2O_4 + CO_2 + H_2O$$

Rising costs of zinc metal and adverse pollution regulations will shift manufacture away from the zinc process. Over the long term sodium hydrosulfite will be manufactured by the amalgam or formate process.

SODIUM SULFIDE

USES AND ECONOMICS. Sodium sulfide is an inorganic chemical that has attained an important position in the organic chemical industry. It is consumed as a reducing agent in the manufacture of amino compounds, and it enters into the preparation of many dyes. It is also employed extensively in the leather industry as a depilatory. Sodium polysulfide is one of the necessary reactants for making Thiokol synthetic rubber. Other industries where its use is important are the rayon, metallurgical, photographic, and engraving fields.

MANUFACTURE. This chemical may be obtained as 30% crystals of sodium sulfide or as 62% flakes. Solutions of it may be shipped in steel. One disadvantageous property of sodium sulfide is its deliquescence. It crystallizes with nine molecules of water, $Na_2S \cdot 9H_2O$. The oldest method of production is the reduction of sodium sulfate with powdered coal in a reverberatory furnace. Another similar process is the reduction of barite in the same manner, leaching, and double decomposition with soda ash. For the reactions involving the reduction of salt cake, very drastic conditions are needed. The reaction must be carried out above 900°C. The reactions are:

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$$
$$Na_2SO_4 + 4CO \rightarrow Na_2S + 4CO_2$$

Specially designed small reverberatory furnaces seem to give the least difficulty, because they avoid overheating the charge. The reaction takes place in the liquid phase and is very rapid. Rotary kilns of the type used for calcining limestone have been applied with some success to this reaction. The reduction of barium sulfate is very similar. Newer plants use nickel or nickel-clad equipment to reduce iron contamination. The substance issuing from the furnace is known as *black ash*.

Another method of production involves the saturation of a caustic soda solution with hydrogen sulfide and the addition of another molecule of sodium hydroxide according to the reactions:

$$H_2S + NaOH \rightarrow NaHS + H_2O$$
$$NaHS + NaOH \rightarrow Na_2S + H_2O$$

Heavy-metal sulfides are filtered from the solution of sodium hydrosulfide. The solution is concentrated and then reacted with sodium hydroxide to give a high-purity product. Stainless steel is used as a construction material.

SODIUM HYDROSULFIDE

USES AND ECONOMICS. Sodium hydrosulfide (NaHS) finds use in ore flotation (30 percent), dyestuff processing (20 percent), as a leather depilatory (20 percent), the manufacture of rayon and organic chemicals (10 percent) and in the metallurgical industry. There were five merchant producers who operated six plants in 1981. Total demand was about 18,000 t/year.

MANUFACTURE. This chemical may be obtained as a 44 to 46% liquid or as a 72 to 75% flaked material. It is made by treating sodium hydroxide solution with hydrogen sulfide or is obtained as a so-called by-product in the manufacture of carbon disulfide, where a mixture of carbon disulfide and hydrogen sulfide gases is treated with sodium hydroxide to produce sodium hydrosulfide and carbon disulfide. Mercaptans may also be formed with the hydrocarbons, so this product cannot be used in all applications.

SODIUM THIOSULFATE

USES AND ECONOMICS. Sodium thiosulfate crystallizes in large, transparent, extremely soluble prisms with five molecules of water. It is a mild reducing agent, like sodium sulfite. It is employed as an antichlor following the bleaching of cellulose products and as a source of sulfur dioxide in the bleaching of wool, oil, and ivory. In photography, which accounts for 90 percent of current use, it is used to dissolve unaltered silver halogen compounds from negatives and prints, where it is commonly called "hypo." It is a preservative against fermentation in dyeing and serves in the preparation of mordants. Other minor uses of sodium thiosulfate are in the reduction of indigo, in the preparation of cinnabar, in the preparation of silvering solutions, and in medicine.

Use of the sodium salt is slowly declining, especially in the photography business, where gains are being made by ammonium thiosulfate.

MANUFACTURE. Of the several methods for the production of sodium thiosulfate, the most important is from sodium sulfite and free sulfur:

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

The resulting liquor is concentrated and crystallized. The crystals formed ($Na_2S_2O_3 \cdot 5H_2O$) are immediately packed in airtight containers to prevent efflorescence. A second method of preparation is from sodium sulfide. Sulfur dioxide is passed into a solution of sodium sulfide and sodium carbonate of low concentration (not more than 10% each):

$$Na_2CO_3 + 2Na_2S + 4SO_2 \rightarrow 3Na_2S_2O_3 + CO_2$$

The sodium thiosulfate is obtained by evaporation and crystallization.

SODIUM NITRITE

USES AND MANUFACTURE. From the standpoint of the dye industry, sodium nitrite is a very important chemical. Here it is employed for the diazotization of amines in making azo dyes. It is used in meat processing as a preservative to prevent botulism, and when mixed with

sodium nitrate it is employed in metal treatment. It is also used as a bleach for fibers, in photography, and in medicine. Formerly, it was prepared by the reaction

$$NaNO_3 + Pb \rightarrow NaNO_2 + PbO$$

Sodium nitrite is now manufactured by passing the oxidation product of ammonia into a soda ash solution.

$$Na_2CO_3 + 2NO + \tfrac{1}{2}O_2 \rightarrow 2NaNO_2 + CO_2$$

Any sodium nitrate also formed may be separated by crystallization.

SODIUM SILICATES[8]

USES AND ECONOMICS. Sodium silicates are unique in that the ratio of their constituent parts, Na_2O and SiO_2, may be varied to obtain desired properties. At the present time there are more than 40 varieties of commercial sodium silicates, each with a specific use. Silicates that have a molar ratio of $1Na_2O/1.6SiO_2$ to $1Na_2O/4SiO_2$ are called colloidal silicates. Sodium metasilicate (Na_2SiO_3) has a ratio of 1 mol of Na_2O to 1 mol of SiO_2. A compound with a higher content of Na_2O, with 1½ mol of Na_2O to 1 mol of SiO_2, is called sodium sesquisilicate ($Na_4SiO_4 \cdot Na_2SiO_3 \cdot 11H_2O$). Another compound still higher in Na_2O content is sodium orthosilicate (Na_4SiO_4), which contains 2 mol of Na_2O to 1 mol of SiO_2.

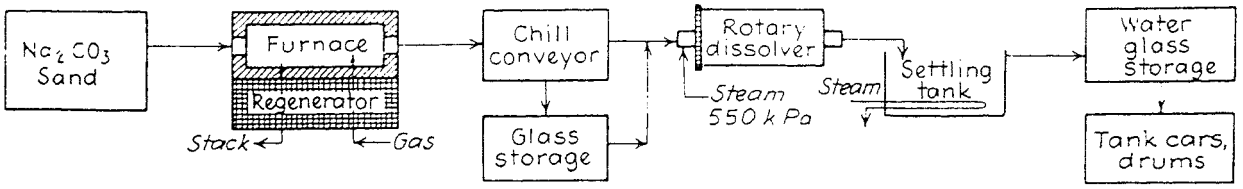
A major use is in the manufacture of silica-based catalysts and silica gels. Other significant uses are in the production of soaps and detergents, pigments, and adhesives, metal cleaning, and water and paper treatment. A large percentage of lower colloidal silicates (water glass) is sold as 32 to 47% solutions employed as adhesives for many kinds of materials, especially paperboard used in corrugated containers. These solutions are also consumed alone or in mixtures with many other materials, e.g., as adhesives for plywoods, wallboard, flooring and metal foils. Sodium metasilicate exists in the hydrated form and is sold as a solid. It is more alkaline than soda ash and is used in metal cleaning and as a strongly alkaline detergent. Sodium sesquisilicate and sodium orthosilicate are employed in the same fields as metasilicates but where a more strongly alkaline product is needed. Demand for silicates in 1980 was 665,000 t. There were 10 producers and 33 producing plants.

MANUFACTURE. These silicates are made by fusing sodium carbonate and silica (sand) in a furnace resembling that used for the manufacture of glass, as shown in Fig. 9.3. The reaction takes place at about 1400°C.

$$Na_2CO_3 + nSiO_2 \rightarrow Na_2O \cdot nSiO_2 + CO_2$$

In the most common commercial silicates n equals 2.0 or 3.2. Intermediate compositions are obtained by mixing, and more alkaline ratios by adding caustic soda or by initially fusing the sand with caustic soda. The product upon cooling forms a clear, light bluish-green glass. The color is due to impurities of less than 1%, usually iron. If the material is to be sold as a solution, the product is ground and dissolved in water or by steam under pressure when the ratio of silica to alkali is above 2. This procedure is shown in Fig. 9.3, but, when liquids are

[8]Vail, *Soluble Silicates*, ACS Monograph 116, Reinhold, New York, 1952.



In order to produce 1 t of 40° water glass, the following materials and utilities are required:

Sodium carbonate (dense, 58%)	156 kg	Water	666 L
		Steam	520 kg
Sand	293 kg	Electricity	85.7 MJ
Gas (1.05 MJ)	156 m^3	Direct labor	2.8–3.3 work-h

Fig. 9.3. Flowchart for the manufacture of sodium silicate.

made directly, the melt flows from the furnace and without chilling passes into an open rotary dissolver where it is hydrated in steam and water not under pressure. The resulting solution from either method is usually sold as concentrated as possible. In the case of $1Na_2O/3 \cdot 2SiO_2$, 43°Bé, or 40% solids, is the upper limit, whereas in the case of $1Na_2O/2SiO_2$, 60°Bé, or 54% solids, is the upper limit. Sodium hydroxide can be substituted for soda ash in the production of silicates. In another process[9] sodium hydroxide, sand, water, and recycle sand slurry are reacted under moderate temperature and pressure to form sodium silicate.

SODIUM PEROXIDE

USES AND ECONOMICS. Sodium peroxide is a pale-yellow, hygroscopic powder. It absorbs moisture from the air and forms a snow-white hydrate, $Na_2O_2 \cdot 8H_2O$. When added to water, this compound forms sodium hydroxide and oxygen. Its principal use is as a powerful oxidizing agent, and its next most important use is in the bleaching of wool, silk, and fine cotton articles and in chemical synthesis. Sodium peroxide reacts with carbon monoxide to form sodium carbonate, and with carbon dioxide to form carbonate with the liberation of oxygen:

$$Na_2O_2 + CO \rightarrow Na_2CO_3$$
$$Na_2O_2 + CO_2 \rightarrow Na_2CO_3 + \tfrac{1}{2}O_2$$

These reactions have led to its use in the regeneration of air in enclosed spaces.

MANUFACTURE. Sodium peroxide is manufactured by burning sodium in an excess of air or oxygen.[10] The product has a purity of about 96%. Care must be taken in handling, since when it is placed on paper or wood, the heat of hydration of the material is sufficient to cause ignition. Fused sodium peroxide reacts with platinum, iron, copper, tin, and brass, but not with nickel. Sodium peroxide reacts violently with ether, glycerin, and glacial acetic acid.

[9]New Liquid-Process Sodium Silicate, *Chem. Eng.* 69 (3), 76 (1962).

[10]Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, vol. II, suppl. II, *The Alkali Metals*, Wiley, New York, 1961.

SODIUM PERBORATE

Sodium perborate is a mild oxidizing agent used in the medical and dental fields. It is recommended as a mouthwash because of its oxidizing and cleansing effects. Other uses are as an oxidizing and bleaching agent for cosmetics, soaps, and textiles. It is made by mixing solutions of borax, sodium peroxide, and hydrogen peroxide and heating the mixture slightly and allowing it to crystallize.

$$Na_2B_4O_7 + Na_2O_2 + 3H_2O_2 \rightarrow 4NaBO_3 + 3H_2O$$

SODIUM AMIDE

Sodium amide is another chemical that has found many special uses in organic chemistry. It is a vigorous dehydrating agent and for this reason is used in the synthesis of indigo and in the preparation of pure hydrazine. It is also an intermediate in the preparation of sodium cyanide and finds application as an aminating agent. It is prepared by passing ammonia into metallic sodium at 200 to 300°C.

$$NH_3 + Na \rightarrow NaNH_2 + \tfrac{1}{2}H_2$$

This compound should be handled with care, since it decomposes explosively in the presence of water. Also, it should not be kept, because disastrous explosions have resulted from handling material that had been stored. It should be consumed as made.

SODIUM CYANIDE AND FERROCYANIDE

Sodium cyanide is not only important in the inorganic and organic chemical fields but also has many metallurgical applications. It is used in treating gold ore, in the case-hardening of steel, in electroplating, in organic reactions, in the preparation of hydrocyanic acid, and in making adiponitrile. Sodium cyanide can be made from sodium amide heated with carbon at 800°C, the carbon as charcoal being thrown into the molten sodium amide. It is first converted to sodium cyanamide:

$$2NaNH_2 + C \xrightarrow{600°C} Na_2NCN + 2H_2$$

$$Na_2NCN + C \xrightarrow{800°C} 2NaCN$$

Another method of manufacture is to melt sodium chloride and calcium cyanamide together in an electric furnace. A commercial method consists of neutralizing hydrocyanic acid with caustic soda:

$$HCN + NaOH \rightarrow NaCN + H_2O$$

Sodium ferrocyanide is manufactured from a crude sodium cyanide made from calcium cyanamide by fusion with sodium chloride in an electric furnace. The ferrocyanide reaction

is carried out in a hot aqueous solution with ferrous sulfate. Soluble sodium and calcium ferrocyanides are formed, and calcium sulfate is precipitated. The calcium ferrocyanide is changed to the sodium salt by the addition of soda ash, precipitating calcium carbonate. The slurry is filtered and washed, and the decahydrate, $Na_4Fe(CN)_6 \cdot 10H_2O$, crystallizes out on cooling.

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Chapter 10

Chlor-alkali Industries: Soda Ash, Caustic Soda, Chlorine

The manufacture of soda ash, caustic soda, and chlorine is one of the most important heavy chemical industries.[1] These chemicals rank close to sulfuric acid and ammonia in magnitude of dollar value of use. The applications are so diverse that hardly a consumer product is sold that is not dependent at some stage in its manufacture on chlorine and alkalies. The three products are sold almost entirely to industry for the production of soap and detergents, fibers and plastics, glass, petrochemicals, pulp and paper, fertilizers, explosives, solvents, and other chemicals.

HISTORICAL. The present synthetic process for the manufacture of soda ash is the Solvay process. Before this method was developed, the LeBlanc (1773) process was in universal use. It was based on roasting salt cake with carbon and limestone in a rotary furnace and subsequent leaching of the product with water. The crude product of the reaction was called *black-ash*. It was leached cold; whereupon some hydrolysis of sulfides took place. These were changed to carbonate by treatment with the carbon dioxide–containing gases from the black-ash furnace. The resulting sodium carbonate solution was concentrated to obtain crystalline sodium carbonate,[2] which was then dried or calcined. No LeBlanc process plant was ever built in the United States, and none is now being operated anywhere in the world. In 1861 Ernest Solvay began developing the ammonia-soda process. At first this method had great difficulty in competing with the older and well-established LeBlanc process, but in a few years the Solvay process reduced the price of soda ash almost one-third. After a struggle during which the producers of LeBlanc soda used price cutting to attempt to stifle competition, the ammonia-soda process completely displaced the LeBlanc by 1915.

The Solvay process continues to be of interest in Europe and countries without deposits of natural sodium carbonate, but by 1982, only one Solvay plant continues to operate in the

[1]ECT, 3d ed, vol. 1, 1978, p. 799; Hou, *Manufacture of Soda*, 2d ed., Reinhold, New York, 1942.

[2]A flowchart of this obsolete process is given in Badger and Baker, *Inorganic Chemical Technology*, 2d ed., McGraw-Hill, New York, 1941, p. 137.

***Table* 10.1** United States Production of Soda Ash (in thousands of metric tons per year)

Year	Ammonia-Soda Process (Solvay)	Natural Sodium Carbonate	Total
1965	4478	1358	5836
1970	3994	2435	6429
1975	2547	3957	6504
1976	2131	4742	6873
1977	1645	5562	7207
1978		6160	
1979		7545	
1980		7540	
1981		7760	9200
1982		7500*	8690

*Estimated

SOURCES. *Statistical Abstract of the United States*, 101st ed.; *Chem. Eng. News*, 59 (9) 15 (1981); 60 (9) 13 (1982); and 61 (9) 25 (1983).

United States. It is kept alive by low installed cost and high freight rates. "Natural" soda from the Wyoming deposits now dominates the domestic market and has a brisk export trade as well. It requires 18.4 GJ of energy to make 1 t of soda ash by the Solvay process, but only 8.4 GJ to produce a metric ton of natural soda ash so energy costs favor mining.[2a] See Table 10.1 for sodium carbonate production figures.

Caustic soda was originally made by batchwise causticization of LeBlanc soda (ash) with lime:

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + \underline{CaCO_3}$$

depending upon the fact that calcium carbonate is almost insoluble in caustic solution.

The electrolytic production of caustic soda was known in the eighteenth century, but it was not until 1890 that caustic was actually produced in this way for industrial consumption. Until shortly before World War I, the amount of caustic soda sold as a coproduct of chlorine from the electrolytic process was almost negligible compared with that made from soda ash by lime causticization. In 1940, however, electrolytic caustic began to exceed lime-soda caustic, and by 1962 the latter had almost disappeared. Figure 10.4 shows the broad usage of caustic soda.

The first patent connected with an industrial use of chlorine is dated 1799 (a quarter century after its discovery) and was for bleaching. Chlorine was made from hydrochloric acid by the Deacon process, which does not have a satisfactory equilibrium:

$$2\,HCl + \tfrac{1}{2}O_2 = H_2O + Cl_2$$

The Weldon process was also used; it conducted the oxidation of HCl with expensive manganese dioxide.

[2a] t = 1000 kg.

Development of high-capacity direct-current electrical generating equipment toward the end of the nineteenth century made the causticization process obsolete and, by the middle of the twentieth century, more than 99 percent of the world's chlorine was produced by the electrolytic process (Table 10.2).

USES AND ECONOMICS. *Soda ash* is a lightweight solid, moderately soluble in water, usually containing 99.3% Na_2CO_3. It is sold on the basis of its sodium oxide content, which is generally 58%. Figure 10.1 and Table 10.3 summarize the more important uses. The production of soda ash from natural trona deposits now exceeds that from ammonia-soda. The synthetic process has been plagued by high costs and pollution problems and is disappearing in the United States.

Pure caustic soda is a brittle white solid that readily absorbs moisture and carbon dioxide from the air. It is sold on the basis of its Na_2O content and usually contains about 76% Na_2O equivalent to 98% NaOH. The term caustic soda is widely used because this compound is corrosive to the skin. Table 10.4 presents its diversified distribution. The traditional uses in the fields of soap, textiles, and petroleum refining are still substantial, and there is increasing use in the field of chemicals.

Since the ratio of NaOH to Cl_2 manufactured is fixed by the proportions in NaCl, a difficult marketing problem constantly exists. Currently, caustic is in strong demand and expected to remain so, but during the last decade, chlorine demand has often exceeded the supply. The problems of storage of chlorine and storage or disposal costs for excess caustic have frequently made the markets very volatile.

Chlorine, originally used almost entirely for bleaching, has increased in importance extremely fast. This is largely due to its use in the synthesis of organic chemicals, in many of which it does not appear in the end product but enters into the intermediate steps. Table 10.2 shows the production of chlorine in the United States.

Table 10.5 reviews the consumption of chlorine. Metallurgical uses include not only the beneficiation of ores and fluxing, but also the extraction of copper, lead, nickel, gold, and platinum. The end products include such items as clothing, jewelry, paints, foods, paper, tires, and toys.

***Table* 10.2** U.S. Production of Caustic Soda and Chlorine (in metric kilotons)

Year	Caustic Soda (100%) (NaOH)	Chlorine
1960	4,356	4,215
1965	6,220	5,925
1970	9,219	8,876
1975	8,454	8,334
1976	9,079	9,435
1978	10,296	10,047
1979	11,273	11,027
1980	10,600	10,450
1981	9,910	9,730
1982	8,450	8,360

SOURCE: *Chem. Eng. News*, **59** (9) 13, 14 (1981), 60 (9) 12 (1982); **61** (9) 25 (1983).

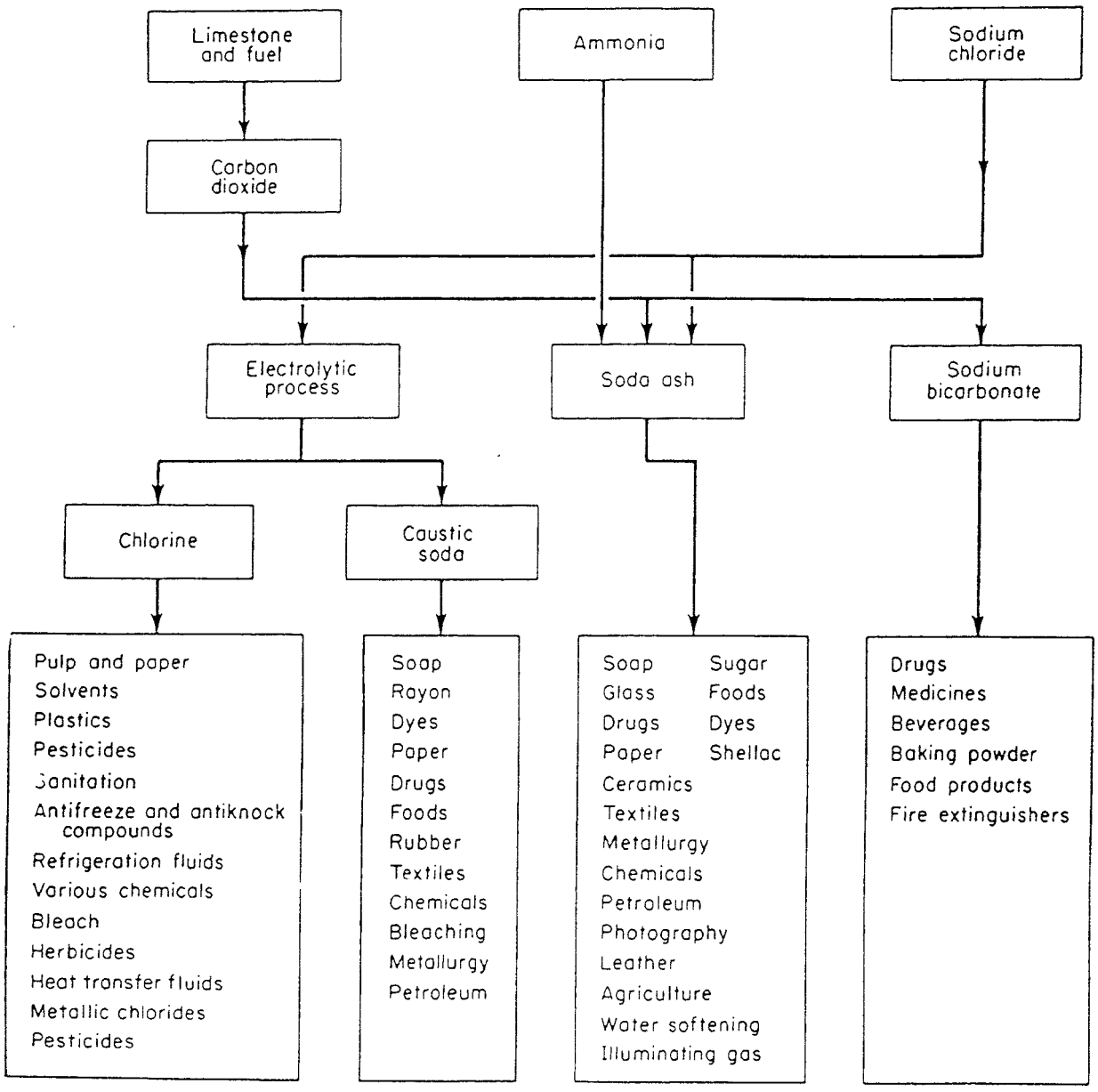

Fig. 10.1. Chlor-alkali industries chart.

***Table* 10.3** Estimated Distribution of Soda Ash in the United States (for 1981)

Consuming Industry	Metric Kilotons per Year	%
Glass	4150	50
Manufacture of chemicals	1735	18
Soap and detergents	377	5
Pulp and paper	226	3
Water and sewage treatment	226	3
Miscellaneous (incl. exports)	830	21
Total	7544	100

SOURCE: *Chem. Week* **129** (24) 68 (1981).

***Table* 10.4** Distribution of Caustic Soda Use in the United States

Consuming Industry	Metric Kilotons per Year	%
Chemical manufacturing	5,783	50
Pulp and paper	2,374	20
Cleaning products	733	6
Rayon and mercerized cotton	500	4
Oil and gas treating	570	5
Miscellaneous	1,676	15
Total	11,636	100

***Table* 10.5** Distribution of Chlorine Consumption in the United States

Consuming Industry	Metric Kilotons per Year	%
Vinyl chloride	1500	17
Chloroethanes	1200	14
Pulp and paper	1100	13
Inorganic chemicals	900	10
Fluorocarbons	800	9
Propylene oxide	800	9
Miscellaneous organics	800	9
Methylene chloride	300	3
Waste water treatment	500	6
Miscellaneous	800	9
Total	8700	99

MANUFACTURE OF SODA ASH

The Solvay process uses salt, limestone, and coke or natural gas as its raw materials and uses ammonia as a cyclic reagent. Its success depends upon the fact that ammonia, carbon dioxide, and water in the proper proportions react to form ammonium bicarbonate, which reacts with sodium chloride to form sodium bicarbonate, which is relatively insoluble in the solution used and can be filtered out and roasted to form soda ash. The ammonium chloride formed is converted back to ammonia by reaction with lime, the calcium chloride thus formed being the principal pollutant from the process. This fine old process is described in detail in the fourth edition of this book.

The Green River Basin of southwestern Wyoming is underlaid with huge deposits of trona, naturally occurring sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$); some is also found in dry lakes in California. The Wyoming beds are worked by conventional underground mining techniques, although a plant using solution mining is slated to start up in 1982. Solution mining is expected to lower costs substantially, increasing exports and making the position of Solvay plants even more difficult. Very little processing of trona is required.[3] Solution, clari-

[3]Sommers, Soda Ash from Trona, *Chem. Eng. Prog.* 56 (2) 76 (1960).

fication, filtration, crystallization, drying, and calcining suffice. Depending on temperature and CO_2 concentration, sesquicarbonate, sodium carbonate monohydrate, or sodium bicarbonate can be the final product. Borax-containing brines from Searles Lake[4] are also being processed for soda ash by a carbonation process as illustrated in Fig. 10.2. Carbonation is under a pressure of 93 KPa. Carbonation converts the carbonate present to bicarbonate, which is then flushed of brine salts, dried, and heated. This drives off CO_2, which is reused. Additional CO_2 is recovered from the boiler plant flue gas by absorption with monoethanolamine solution. Bleaching with $NaNO_3$ and high-temperature burning produces a white product. While there is a market for both light and dense sodium carbonate, the light material (640 kg/m^3) is ordinarily too bulky to ship economically, so a final treatment produces dense (993 kg/m^3) material.

MANUFACTURE OF SODIUM BICARBONATE

Sodium bicarbonate, or baking soda, is made by treating a saturated solution of soda ash with CO_2 in a contacting tower at about 40°C. The suspension of bicarbonate formed is removed from the bottom of the tower, filtered, and washed on a rotary drum filter. The cake is then centrifuged and dried on a continuous belt conveyor at 70°C. Bicarbonate made in this fashion is about 99.9% pure. Sodium bicarbonate is widely used in the food industry, in making rubber, in pharmaceuticals as an antacid, in fire extinguishers, soap and detergents, rug cleaners, animal feeds, and textiles, in leather and paper manufacturing, for flue-gas scrubbing, and for many other diversified small-scale uses. The manufacturing capacity in the United States was 250,000 t/year in 1980.

The Piceance Basin of Colorado has nahcolite (natural sodium bicarbonate) beds among

[4]Parkinson, Soda Ash Plant Exploits Mineral-Laden Brine, *Chem. Eng.* 84 (24) 62 (1977).

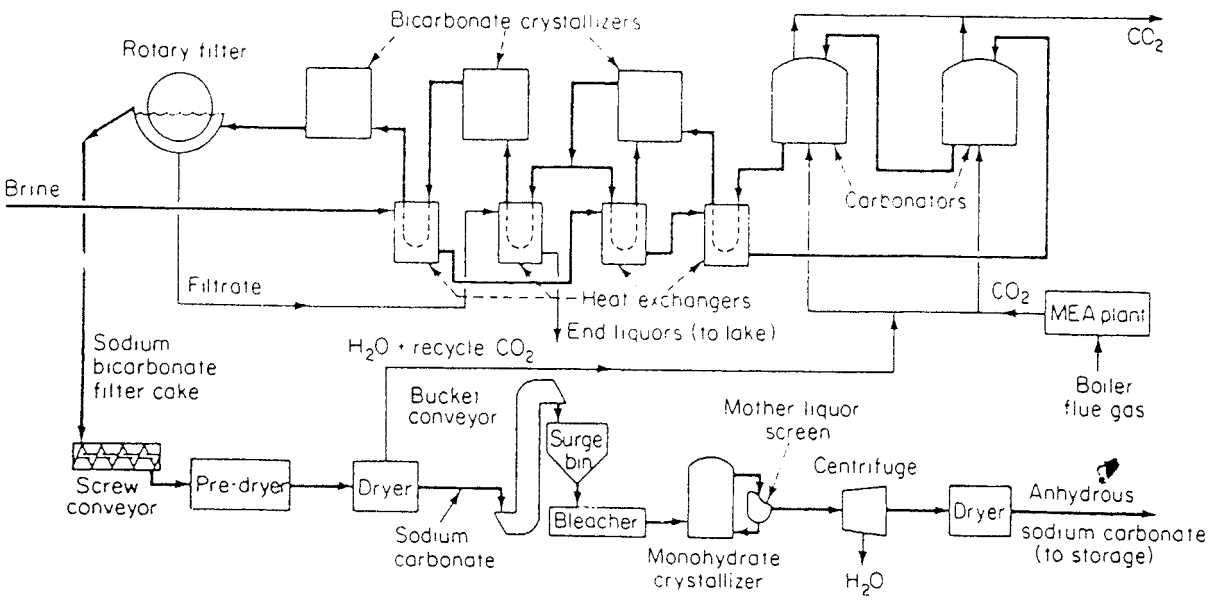

Fig. 10.2. The Kerr-McGee soda ash plant will process 38 m^3/min of brine.

the oil-shale deposits. A project is underway to recover this by underground dry mining. The crude material could be used directly for flue-gas scrubbing to remove sulfur dioxide, or as an additive for animal feed.

MISCELLANEOUS ALKALIES

Various alkalies of different strengths are consumed commercially, according to the contained amounts of NaOH, Na_2CO_3, or $NaHCO_3$. Some of these are mechanical mixtures, such as *causticized soda ash* (soda ash with 10 to 50% caustic) for bottle washing and metal cleaning, and *modified sodas* (soda ash with 25 to 75% $NaHCO_3$) for mild-alkali demands, as in the tanning industry. *Sodium sesquicarbonate*, or the natural mineral trona, is very stable and can be used without modification. It finds use in wool scouring and in laundering. *Sal soda* ($Na_2CO_3 \cdot 10H_2O$) is also known as *washing soda* or *soda crystals*. This material tends to lose water to the air on storage and to change drastically in appearance.

MANUFACTURE OF CHLORINE AND CAUSTIC SODA

Chlorine and caustic soda are produced almost entirely by the electrolysis of aqueous solutions of alkali metal chlorides, or from fused chlorides. Brine electrolysis produces chlorine at the anode and hydrogen along with the alkali hydroxide at the cathode. If chlorine and the alkali hydroxide are to be the final product, cell design must keep them from mixing. Many ingenious designs have been invented for practical cells. At the present, three types dominate the industry, the diaphragm cell, the membrane cell, and the mercury cell. There are many variations of each type.

REACTIONS AND ENERGY CHANGES

Decomposition Voltage and Voltage Efficiency. The energy consumed in the electrolysis of the brine is the product of the current flowing and the potential of the cell. The theoretical, or minimum, voltage required for the process may be derived from the Gibbs-Helmholz equation, which expresses the relation between the electric energy and the heat of reaction of a system.[5]

$$E = \frac{-J\Delta H}{nF} + \frac{T\,dE}{dT}$$

where E = theoretical decomposition voltage
ΔH = enthalpy change of reaction
J = electrical equivalent of heat
T = absolute temperature
F = Faraday constant
n = number of equivalents involved

[5]Perry, 5th ed., p. 4.

The heat of reaction for the electrolysis of salt may be found from the heats of formation of the components of the overall reaction, which is:

$$NaCl\ (aq) + H_2O\ (l) \rightarrow NaOH\ (aq) + \tfrac{1}{2}H_2\ (g) + \tfrac{1}{2}Cl_2\ (g)$$

This may be broken down to the following reactions for formation:

$$Na\ (s) + \tfrac{1}{2}Cl_2\ (g) \rightarrow NaCl\ (aq) \qquad \Delta H = 407\ kJ$$
$$H_2\ (g) + \tfrac{1}{2}O_2\ (g) \rightarrow H_2O\ (l) \qquad \Delta H = 286\ kJ$$
$$Na\ (s) + \tfrac{1}{2}O_2\ (g) + \tfrac{1}{2}H_2\ (g) \rightarrow NaOH\ (aq) \qquad \Delta H = 469\ kJ$$

The net ΔH for the overall reaction results from

$$+407 + 286 - 469 = 224\ kJ$$

When this value of ΔH is substituted in the Gibbs-Helmholz equation and the change in voltage with temperature is neglected, the value of E is found to be 2.31 V. The omission of $T\,dE/dT$ involves an error of less than 10 percent for most cells.

The ratio of this theoretical voltage to that actually used is the *voltage efficiency* of the cell. Voltage efficiencies range from 60 to 75 percent. According to Faraday's law, 96,500 C of electricity passing through a cell produce 1 gram-equivalent of chemical reaction at each electrode. Because of side reactions, cells usually require more than this amount. The ratio of the theoretical to the actual current consumed is defined as the *current efficiency*. Current efficiencies run 95 to 97 percent and, unless otherwise specified, are understood to be *cathode* current efficiencies. The current divided by the area on which the current acts is known as the *current density*. A high value is desirable. The product of voltage efficiency and current efficiency is the *energy efficiency* of the cell. Another consideration is the *decomposition efficiency*, which is the ratio of equivalents produced in the cell to equivalents charged. In the usual commercial cell, this decomposition efficiency is about 60 to 65 percent. Some newer, larger membrane cells claim efficiencies as high as 75 to 80 percent. Diaphragm cells operated to obtain very high decomposition efficiencies encounter difficulties with the migration of hydroxyl ions back to the anode, resulting in the formation of hypochlorite ion. Hydroxyl ions are decomposed on the anode by the reaction

$$2OH^- \rightarrow H_2O + \tfrac{1}{2}O_2 + 2e$$

The oxygen formed reacts with the graphite of the anodes, causing decreased anode life. In cells with metal anodes, the oxygen does not react.

CELL TYPES. Only a few years ago, it seemed that the mercury cell would soon dominate the field because of the high quality of its product and the reduced evaporation required, but unexpected difficulties arose. Mercury discharge into nearby waters, although small in quantity, was found to be the source of methyl mercury, which caused a particularly debilitating disease first observed in Japanese children. This connection led to drastic reductions in the permissible discharge of mercury into either air or water, and now has led some countries to prohibit production with mercury cells entirely. Improved designs of membrane cells and newer and cheaper purification techniques have reduced costs and improved efficiencies to the point that the membrane cell with dimensionally stable titanium anodes now appears to be about to dominate the field. In this slow-growing business, changes will come about slowly.

In 1979, 50 percent of world production[6] was by mercury cells and 49 percent by diaphragm cells. In the United States 74.3 percent of the plants used diaphragm cells and 20.3 percent mercury cells. In Japan, where mercury cells must be totally replaced by 1984, membrane cells will most certainly be the technique of choice.

Nothing stimulates process improvement like competition so severe that existence is threatened, thus mercury and diaphragm cells will probably be quickly improved and should be around for a long time.

Diaphragm Cells

Diaphragm cells contain a diaphragm, usually made of asbestos fibers, to separate the anode from the cathode. This allows ions to pass through by electrical migration but reduces the diffusion of products. Anodes have usually been made of graphite, cathodes of cast iron. Diaphragms permit the construction of compact cells of lowered resistance because the electrodes can be placed close together. The diaphragms become clogged with use, as indicated by higher voltage drop and higher hydrostatic pressure on the brine feed. They must be replaced regularly. The diaphragm permits a flow of brine from anode to cathode and thus greatly lessens or prevents side reactions (e.g., sodium hypochlorite formation). Cells with metal cathodes (titanium coated with rare earth oxides, platinum or noble metals, or oxides) rarely develop clogged diaphragms and operate for 12 to 24 months without requiring diaphragm replacements. It is expected that diaphragms made of corrosion-resistant plastics will increase service life and remove the environmentalist's objection to any process that may release asbestos fibers into the environment. Figure 10.3 shows a modern monopolar diaphragm cell, and Fig. 10.4 a cell room.

[6]Savage, *Chem. Eng.* 86 (24) 63 (1979).

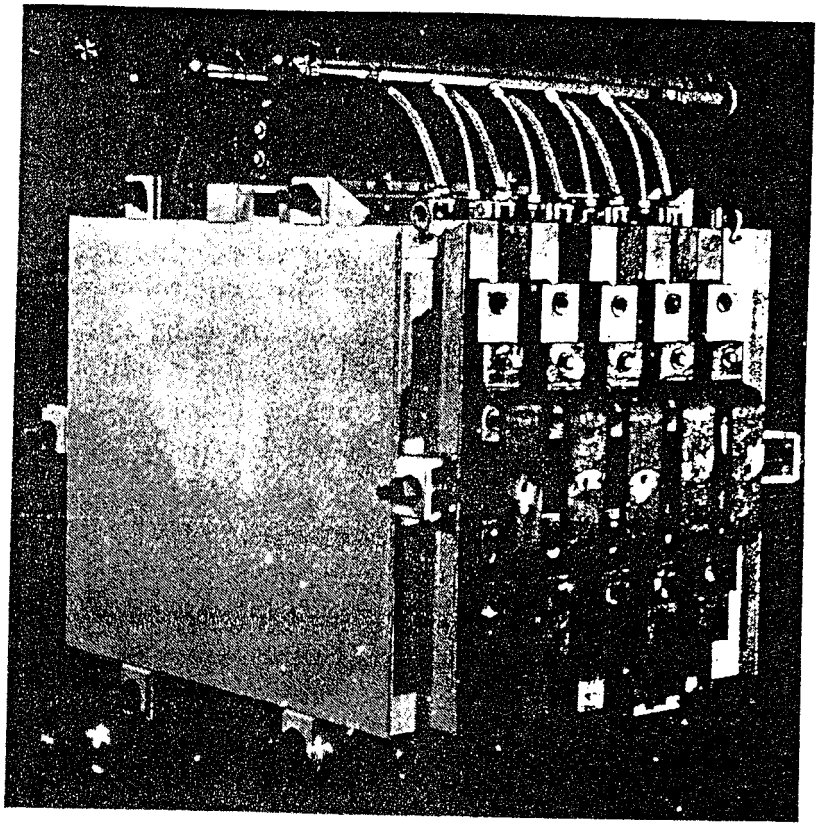

Fig. 10.3. Monopolar caustic-chlorine cell. *(Courtesy of Diamond Shamrock Corp.)*

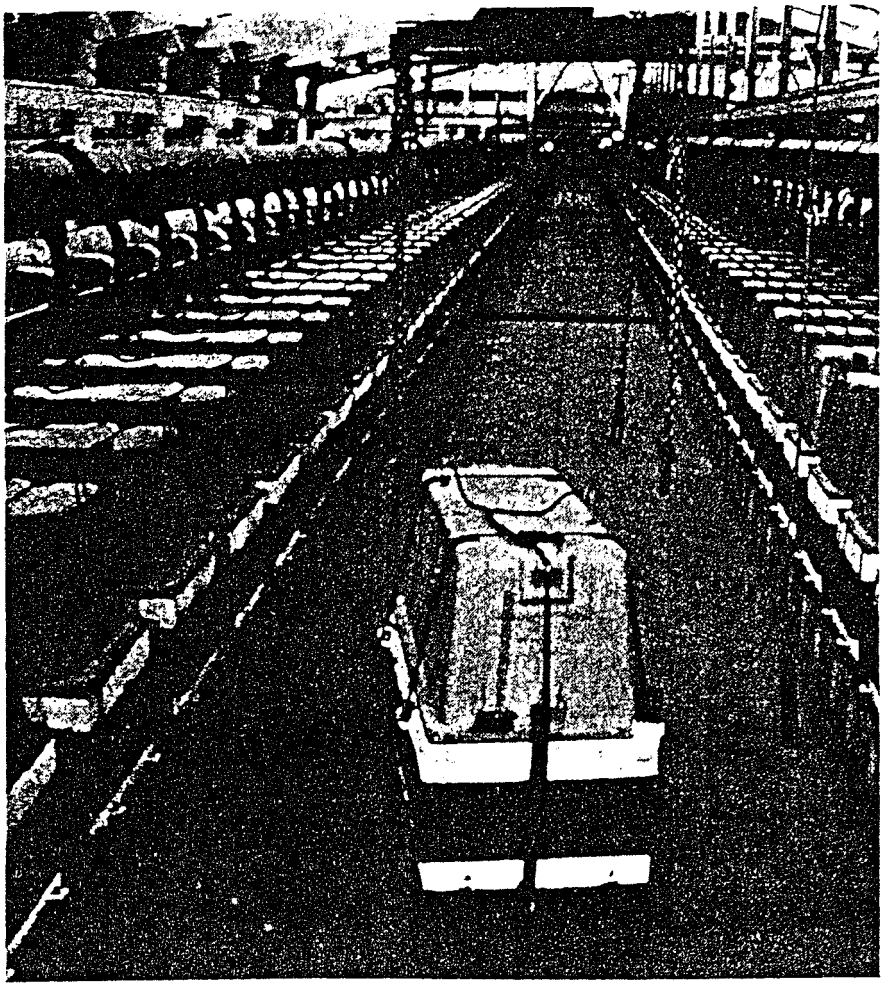

Fig. 10.4. Caustic-chlorine diaphragm cell room. *(Courtesy of Diamond Shamrock Corp.)*

A major advantage of the diaphragm cell is that it can run on dilute (20%), fairly impure brine. Such dilute brines produce dilute sodium hydroxide (typically 11% NaOH with 15% NaCl) contaminated with sodium chloride as a product. Concentration to the usual shipping strength of 50% is required, and this consumes a great deal of energy even when multiple-effect evaporators are used. Approximately 2600 kg of water must be evaporated to produce a ton of 50% caustic. Although salt is not very soluble in concentrated caustic solution, the small amount of chloride ion which remains is highly objectionable to some industries (e.g., rayon manufacture). Sodium chlorate is also objectionable when caustic is to be used in the manufacture of glycerin, pentaerythritol, sodium sulfate, sodium hydrosulfate, cellophane, and several other chemicals. A catalytic reduction[7] with hydrogen can remove this without resorting to ammonia extraction.

Membrane Cells

Membrane cells use a semipermeable membrane to separate the anode and cathode compartments. With diaphragm cells, back migration of ions is controlled by the rate of flow of

[7]Mitchell and Modan, Catalytic Purification of Diaphragm Cell Caustic, *Chem. Eng.* 86 (5) 88 (1979).

fluid through the diaphragm, and this is regulated by careful control of liquid levels in the compartments. Membrane cells[8] separate the compartments with porous chemically active plastic sheets that allow sodium ions to pass but reject hydroxyl ions. Several polymers have been developed for this demanding service. DuPont has developed a perfluorosulfonic acid polymer (Nafion), while Ashai uses a multiple-layer membrane of perfluorosulfonic acid polymer coated on one side with a perfluorocarboxylic acid polymer. The purpose of the membrane is to exclude OH^- and Cl^- ions from the anode chamber, thus making the product far lower in salt than that from a diaphragm cell. Membrane cells operate using a more concentrated brine and produce a purer, more concentrated product (28% NaOH containing 50 ppm of NaCl; 40% NaOH product has recently been claimed[9]). Such product requires only 715 kg of water to be evaporated to produce a metric ton of 50% caustic; a considerable saving. Because of the difficulty and expense of concentration and purification, only large diaphragm cell installations are feasible. Membrane cells, producing relatively concentrated NaOH offer the possibility of operation at the point of caustic use, thus saving freight. Small, efficient units may cause a revolution in the distribution of the chlor-alkali industry, particularly if efficiencies remain high in small units. No commercial-sized membrane units were operating in the United States in 1982.

Serious suggestions have been made[10] that a combination plant using the output of the membrane cells as feed to the diaphragm cells might result in the optimum application of both and make a considerable cost reduction overall. Such combinations have been used with mercury cell output feeding diaphragm cells. Membranes are more readily clogged than diaphragms, so some of the savings are lost because of the necessity to pretreat the brine fed in order to remove calcium and magnesium before the electrolysis.

A membrane cell 20 times larger than former cells is being offered (1981).[11] Such a cell unit can produce 240 t of chlorine per year, and power consumption is substantially reduced below either mercury or diaphragm cells. A bipolar cell unit is capable of producing 20,000 t/year with a current density of 4 kA/m^2.

Mercury Cells

Mercury cells operate quite differently from the other types. The anodes remain either graphite or modified titanium as before, but the cathode is a flowing pool of mercury. The electrolysis produces a mercury-sodium alloy (amalgam) which is not decomposed by the brine present. The amalgam is decomposed in a separate vessel according to the reaction

$$2Na \cdot Hg + 2H_2O \rightarrow 2NaOH + H_2 + Hg$$

When exactly the correct amount of water is used, 50% NaOH with a very low salt content (30 ppm) becomes the direct product with no evaporation required. The small loss of mercury to the environment presents extreme problems.

Japan outlawed mercury cell use after 1975 (later extended to 1984). Although major reductions in the mercury discharged had taken place, the construction of mercury cells in

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[8]Chlor-alkali Membrane Cell Set for Market, *Chem. Eng. News* 56 (12) 20 (1978).

[9]Ukihashi, A Membrane for Electrolysis, *CHEMTECH* 10 (2) 118 (1980).

[10]Savage, Membrane Cells a Hit with Chlorine Producers, *Chem. Eng.* 86 (24) 63 (1979).

[11]*Chem. Week*, 130 (6) 50 (1982).

the United States came to an abrupt halt. Careful process control, combined with treatment of water and air effluent, may make it possible for mercury plants to meet environmental standards and survive, but most companies are hesitant to erect new units. Diaphragm cells and membrane cells use about the same amount of electrical energy, mercury cells somewhat more. The ratio is approximately 3:4.

HYBRID FUEL CELLS. The hydrogen from any type of cell can be reacted in an efficient fuel cell to produce a significant amount of electrical energy. If this energy is used for electrolysis, costs should be reduced around 20 percent. This development is expected to take place during the next decade.

Other Processes

Other processes for making chlorine include the Downs cell (for making sodium, Chap. 11), caustic potash manufacture, hydrogen chloride decomposition (Chap. 11), the nitrosyl chloride process, and the process where salt is treated with nitric acid to form sodium nitrate and chlorine with nitrosyl chloride (containing 4 to 10% nitrogen tetroxide) as a by-product. The nitrosyl chloride vapor is placed in contact with oxygen to produce nitrogen tetroxide and chlorine:

$$2NOCl + O_2 \rightarrow N_2O_4 + Cl_2$$

After liquefying and distilling the chlorine out, the nitrogen tetroxide is absorbed in water to make nitric acid and nitrous acids, which are recycled:

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$$

The advantage of this process is that it produces chlorine but no caustic soda. The limited demand for sodium nitrate regulates the amount of chlorine that can be made in this way. The overall reactions may be simplified as follows:

$$3NaCl + 4HNO_3 \rightarrow 3NaNO_3 + Cl_2 + NOCl + 2H_2O$$
$$2NOCl + 3HNO_2 + 3O_2 + H_2O \rightarrow 5HNO_3 + Cl_2$$

DuPont has started up a 550 t/day plant to recover chlorine from hydrogen chloride by the Kel-Chlor[12] process. This process accepts either gaseous or aqueous hydrogen chloride and converts it to chlorine, using a four-step operation based on the Deacon process but involving nitrosyl sulfuric acid ($NHSO_5$) as a catalyst. The development of oxychlorination technology has been the major factor in reducing the oversupply of by-product hydrogen chloride from organic chlorination processes.

Another thermal process[13] designed to produce chlorine from chloride salts without electrolysis reacts sodium chloride with sulfuric acid, then reacts the hydrogen chloride with oxy-

[12]Hydrogen Chloride to Chlorine via the Kel-Chlor Process, *Chem. Eng.* 69 (4) 57 (1974). The Kel-Chlor Process, *Ind. Eng. Chem.* 61 (7) 23 (1969).

[13]*Chem. Eng.* 88 (22) 25 (1981).

gen over a mixed K_2SO_4–V_2O_5 catalyst to form chlorine. Only bench-scale work has been completed. Because of the expected stronger demand for caustic than chlorine, these processes are currently of small interest, but the situation may well change with time.

UNIT OPERATIONS AND CHEMICAL CONVERSIONS

BRINE PURIFICATION. Calcium, iron, and magnesium compounds all tend to plug diaphragms. Precipitation with soda ash and caustic soda is commonly practiced. Additional treatment with phosphates and as yet undisclosed other substances is required for membrane cells. Sulfates may be removed by treatment with barium chloride. Brine is preheated against other streams to reduce energy requirement.

BRINE ELECTROLYSIS. Whatever type of cell is used, 3.0 to 4.5 V per cell are required. When cells are connected in parallel and low voltage is provided to each cell, the connection is known as monopolar. When cells are connected in series, allowing generation and use of power at higher voltages, the cell is said to be bipolar. Smaller bus bars are required for bipolar systems.

EVAPORATION AND SALT SEPARATION. Diaphragm cells discharge a brine containing around 11% NaOH and 15% NaCl. On concentration to 50% NaOH in multiple-effect nickel-tubed evaporators, most of the salt crystallizes out and can be removed for recycling. Where the presence of 1% salt is not objectionable, this 50% solution is shipped as a standard commercial strength. Concentration to 73% caustic solution reduces the shipping cost, but greatly increases the shipping and unloading problem because the high melting point of the concentrated material makes steam-heated lines and steam heating of the tank cars necessary. The melting points are: for 50%, 12°C; for 73%, 65°C.

Membrane cells produce caustic that is much more concentrated than that from diaphragm cells (28 to 40%) and that contains very little chlorine, so less evaporation or treatment is required.

No evaporation is required to produce a 50% solution when mercury cells are used.

FINAL EVAPORATION. Either the cooled and settled 50% caustic or a specially purified caustic may be concentrated in a single-effect final or high evaporator to 70 to 75% NaOH, using steam at 500 to 600 kPa. This very strong caustic must be handled in steam-traced pipes to prevent solidification. It is run to the finishing pots. Another method of dehydrating 50% caustic utilizes the precipitation of NaOH monohydrate. This monohydrate contains less water than the original solution. Precipitation is accomplished by the addition of ammonia to the 50% solution, and this also purifies the caustic. If the 50% solution is treated with anhydrous ammonia,[14] particularly in a countercurrent system, free-flowing anhydrous crystals separate from the resulting aqueous ammonia. This procedure must be carried out in pressure vessels.

FINISHING OF CAUSTIC IN POTS. Although 50% caustic was at one time finished in special close-grained, cast-iron, direct-fired pots, the heat efficiency is so low that good practice now

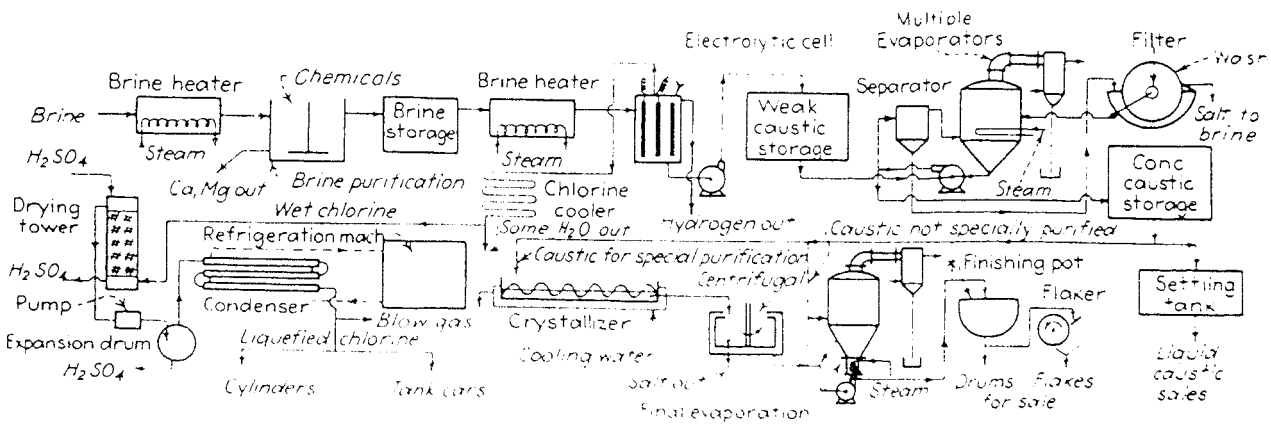
[14]Muskat, Method for Producing Anhydrous Caustic, U.S. Patent 2,196,593 (1940).

handles only 70 to 75% NaOH in this fashion. The final temperature is 500 to 600°C and boils off all but about 1% or less water. These pots are now being replaced by Dowtherm heated evaporators, even above 50%. The hot anhydrous caustic is treated with sulfur to precipitate iron and settled. The product is pumped out by a centrifugal pump that discharges the molten material into thin steel drums holding about 320 kg, or into a flaking machine. Some caustic is made into beads, which some think handle more readily than flakes. All types of solid caustic are more expensive (about 50%) than solutions and have but a small amount of the total market. Much of the solid manufactured goes to exports, because the saving in shipping cost is important.

SPECIAL PURIFICATION OF CAUSTIC. Some of the troublesome impurities in 50% caustic are colloidal iron, NaCl, and $NaClO_3$. The iron is often removed by treating the caustic with 1% by weight of finely divided calcium carbonate and filtering the resulting mixture through a Vallez filter on a calcium carbonate precoat. The chloride and chlorate may be removed by allowing the 50% caustic to drop through a column of 50% aqueous ammonia solution. This treatment produces caustic almost as free of chlorides and chlorates as that made by the mercury process. To reduce the salt content of the caustic necessary for certain uses, it is cooled to 20°C in equipment such as that outlined in Fig. 10.5. Another crystallization method used industrially, however, involves the actual separation of the compound $NaOH \cdot 3\frac{1}{2}H_2O$ or $NaOH \cdot 2H_2O$, leaving the NaCl in the mother liquor. Another procedure reduces the salt content of the caustic soda solution by formation of the slightly soluble complex salt $NaCl \cdot Na_2SO_4 \cdot NaOH$.

A standard process for the continuous extraction of NaCl and $NaClO_3$ in 50% caustic solution is countercurrent extraction in vertical columns with 70 to 95% ammonia. Mercury cells furnish caustic soda essentially free from salt. These purification or manufacturing methods give high grade caustic with less than 1% impurities (anhydrous basis).

CHLORINE DRYING. The hot chlorine evolved from the anode carries much water vapor. It is first cooled to condense most of this vapor and then dried with sulfuric acid in a scrubber



In order to produce 1 t 76% caustic, 879 kg chlorine, and 274.7 m^3 hydrogen (25.2 kg H_2), the following materials and utilities are required:

Salt	1.6 t	Electricity	1197 kJ
Sodium carbonate	29.2 kg	Refrigeration	0.91 t
Sulfuric acid (66°Bé)	100.5 kg	Direct labor	20 work-h
Steam	10.060 kg		

**Daily production is 75.4 t caustic.*

Fig. 10.5. Flowchart for the purification of caustic soda and chlorine using a diaphragm cell.

or tower, as shown in Fig. 10.5. Up to the sulfuric acid tower, the wet chlorine should be handled in polyester, polyvinyl chloride, or similar resistant material; after drying, iron or steel can be employed.

CHLORINE COMPRESSION AND LIQUEFACTION.[15] The dried chlorine is compressed to 240 kPa, or sometimes 550 kPa. For lower pressures, the usual type of compressor employed is the liquid-piston rotary compressor constructed of iron, with concentrated sulfuric acid as the sealing liquid. For larger capacities and higher pressures, centrifugal and nonlubricated reciprocating compressors are chosen. Carbon piston rings or carbon cylinder liners are usually used in the reciprocating compressors, other parts being of cast iron. The heat of compression is removed and the gas condensed. The liquid chlorine is stored in small cylinders, ton cylinders, pipeline, or the 50-t tank cars that are shipped to large consumers. Barges carrying 550 or 1000 t are also employed. There is always some residue, or "blow gas," made up of an equilibrium mixture of chlorine and air. The blow gas is used to make chlorine derivatives, either organic or inorganic, especially bleaching powder.

HYDROGEN DISPOSAL. The hydrogen is frequently made into other compounds, such as hydrochloric acid or ammonia, or is employed for the hydrogenation of organic compounds. It may also be burned for heat generation or used in a fuel cell to produce electricity.

BLEACHING POWDER

A decreasing tonnage of chlorine gas goes into the production of bleaching powder, chiefly because of its instability and the large proportion of inert material. The reaction by which bleaching powder is made is

$$Ca(OH)_2 + Cl_2 \longrightarrow Ca\begin{matrix}O\\ \diagup\\ \\ \diagdown\\ Cl\end{matrix} \cdot H_2O$$

This reaction is carried out below 50°C in a countercurrent fashion by passing chlorine through a rotating steel cylinder with inner lifting blades which shower the solid through the path of the gas. When allowed to stand in the air, the bleaching powder absorbs carbon dioxide. Other inorganic acids will also liberate the HOCl.

$$2CaCl(OCl) + CO_2 + H_2O \rightarrow CaCl_2 + CaCO_3 + 3HClO$$
$$2HClO \rightarrow 2HCl + O_2$$

Simply on standing, however, the following decomposition takes place:

$$2CaCl(OCl) \rightarrow 2CaCl_2 + O_2$$

When dissolved in water, the reaction gives ionized calcium chloride and hypochlorite

$$2CaCl(OCl) \rightarrow 2Ca^{2+} + 2Cl^- + 2OCl^-$$

[15]Eichenhofer and Fedoroff, Chlorine Liquefaction, *Chem. Eng.* 58 (12) 142 (1951).

The OCl^- ion decomposes, liberating oxygen. In general, bleaching powder is an oxidizing agent. Its activity, however, is measured in what is termed *available chlorine*, which is, by definition the weight of chlorine that would exert the same action as the chlorine compound in question. In the case of bleaching powder ($CaOCl_2$) the available chlorine is the same as the percentage of chlorine, but in the case of calcium hypochlorite $Ca(OCl)_2$, the available chlorine is twice the percentage (49.6) of chlorine present (99.2%). This is another way of saying that 1 mol of chlorine is equivalent in oxidizing power to 1 mol of HOCl, or to the ion OCl^-. Bleaching powder by this convention contains about 35% or less of available chlorine when freshly manufactured. The available chlorine concept may be further explained by the reactions:

FOR CALCIUM HYPOCHLORITE

$$Ca(OCl)_2 + 2HCl \rightarrow CaCl_2 + 2HOCl$$

or

$$Ca(OCl)_2 \rightarrow Ca^{2+} + 2OCl^-$$

One mole of bleaching powder will furnish only half this amount of OCl^- ions.

FOR CHLORINE

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

CALCIUM HYPOCHLORITE

Calcium hypochlorite[16] itself may be made in several ways. One method that has been used is the chlorination of calcium hydroxide, as in the manufacture of bleaching powder, followed by the separation of the $Ca(OCl)_2$ through salting out from solution with NaCl. It is also manufactured by the formation under refrigeration of the salt $[Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O]$, which is prepared by the chlorination of a mixture of sodium and calcium hydroxides. This is reacted with a chlorinated lime slurry, filtered to remove salt, and dried, resulting finally in a stable product containing 65 to 70% $Ca(OCl)_2$. The final reaction is:

$$[2Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O] + CaCl_2 + Ca(OCl)_2 \rightarrow 4Ca(OCl)_2 \cdot 2H_2O + 4NaCl + 16H_2O$$

The great advantage of $Ca(OCl)_2$ is that it does not decompose on standing as does bleaching powder. It is also twice as strong as ordinary bleaching powder and is not hygroscopic.

SODIUM HYPOCHLORITE

Sodium hypochlorite is employed as a disinfectant and deodorant in dairies, creameries, water supplies, sewage disposal, and for household purposes. It is also used as a bleach in laundries. During World War I, it was employed in the treatment of wounds as a stabilized

[16]Macmullin and Taylor, U.S. Patent 1,787,048 (1930).

isotonic solution. As a bleaching agent, it is very useful for cotton, linen, jute, rayon, paper pulp, and oranges. Indeed, much of the chlorine bought for bleaching cellulose products is converted to hypochlorite before use. The most common method for making it is the treatment of sodium hydroxide solution with gaseous chlorine.

$$Cl_2 + 2NaOH \rightarrow NaCl + H_2O + NaOCl$$

The other once widely used method was the electrolysis of a concentrated salt solution whereby the same product was made. These electrolytic cells do not have a diaphragm or membrane and are operated at high current density in a nearly neutral solution. The cells are designed to function at low temperature and to bring the cathode caustic soda solution in contact with the chlorine given off at the anode.

SODIUM CHLORITE

Sodium chlorite ($NaClO_2$) was introduced in 1940 by the Mathieson Chemical Co. (now Olin Corp.). The 80% commercial material has about 125% available chlorine. It is manufactured from chlorine through calcium chlorate to chlorine dioxide, ending with the reaction

$$4NaOH + Ca(OH)_2 + C + 4ClO_2 \rightarrow 4NaClO_2 + CaCO_3 + 3H_2O$$

After filtering off the calcium carbonate, the solution of $NaClO_2$ is evaporated and drum-dried. $NaClO_2$ is a powerful but stable oxidizing agent. It is capable of bleaching much of the coloration in cellulosic materials without weakening the cellulose fibers. It finds uses in the pulp and textile industries, particularly in the final whitening of kraft paper. Besides being employed as an oxidizer, $NaClO_2$ is also the source of another chlorine compound, chlorine dioxide, through the reaction

$$NaClO_2 + HCl \rightarrow NaCl + ClO_2$$

Chlorine dioxide has 2½ times the bleaching power of chlorine and is important in water purification, for odor control and for pulp bleaching.

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Chapter 11

Electrolytic Industries

Electrical energy is extensively consumed by the chemical process industries, not only to furnish power through electric motors, but to give rise to elevated temperatures and directly to cause chemical change. Energy in the form of electricity causes chemical reactions that are used by the electrolytic industries described in this chapter.[1] Heat produced by electricity is the source of the high temperature required in the electrothermal industries, which are described in Chap. 12. Most of the electroytic processes have been developed since World War I; few of them are older. The materials manufactured with the aid of electricity vary from chemicals that are also produced by other methods, such as caustic soda, hydrogen, and magnesium, to chemicals that at present cannot be made economically in any other way, such as aluminum and calcium carbide (Table 14.1).

A number of metals other than the aluminum, magnesium, and sodium discussed in this chapter are being made electrolytically. Among these are cadmium, chromium, copper, nickel, titanium, and zinc. Some others are made on a quite small scale. Discussion of the processing of these metals has been arbitrarily omitted, primarily because their processing usually accompanies metallurgical and mining operations instead of chemical processing plants. The cost of electrical power is usually the deciding factor in the electrochemical industries. These industries, therefore, have become established in regions of cheap electrical power, e.g., at Niagara Falls, the Pacific northwest, and Norway. But cheap electric power has tended to vanish as public demand has escalated. This has caused many companies to look beyond the borders of the United States for new plant sites.[2] Table 14.4 indicates the energy needed to produce 1 t of the various materials listed.[2a] Sodium, aluminum, and magnesium can be made economically only by using direct current as a chemical agent. Motor-generator sets, acyclic generators, and mercury-arc rectifiers have been used to make the low-voltage high-amperage currents required but are all obsolete now, although some continue to be used. Since low ripple current is desired, multiple-phase solid-state rectifiers and silicon-controlled rectifiers are the current choices.

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[1]ECT, 3d ed., vol. 5, 1979, p. 375; Newman, Engineering Design of Electrochemical Systems, *Ind. Eng. Chem.* 60 (4) 12 (1968) (85 ref.).

[2]Toth and Lippman, The Quest for Aluminum, *Mech. Eng.* 95 (9) 24 (1973).

[2a]t = 1000 kg.

***Table* 11.1** Chemicals and Metals Made Electrochemically

Material	Process	MJ/kg	Voltage per Cell or Furnace	Yearly Energy Consumption
Alumina, fused	Electrothermal fusion	8–12	100–110	Large
Aluminum	Electrolytic reduction of alumina to aluminum	75–95	5.5–7	Very large
Ammonia, synthetic	Electrolytic hydrogen; pressure hydrogenation	51	—	Small
Cadmium	Electrolytic precipitation of zinc-lead residues	6	2.6	Small
Calcium	Electrothermal reduction	175–190	—	Small
Calcium carbide	Electrothermal reduction	10–11	—	Very large
Calcium cyanamid	Electrothermal reduction	10	—	Large
Caustic soda, chlorine	Electrolysis of brine	10.6	3.4–4.3	Very large
Copper	Copper electrowinning	8–12	1.9–2.4	Large
	Electrolytic refining	0.7–1.3	0.18–0.4	Very large
Ferrochromium, 70%	Electrothermal smelting	16–24	90–120	Large
Ferromanganese, 80%	Electrothermal reduction	12–24	90–115	Very small
Ferromolybdenum, 50%	Electrothermal smelting	24–32	50–150	Small
Ferrosilicon, 50%	Electrothermal smelting	16–28	75–150	Very large
Ferrotungsten, 70%	Electrothermal smelting and refining	12–16	90–120	Small
Ferrovanadium	Electrothermal smelting	16–28	150–250	Small
Gold	Electrolytic refining	1.2	1.3–1.6	Very small
Graphite	Electrothermal change	12–16	80–200	Large
Hydrogen and oxygen	Electrolysis of alkalized water	438	—	Small
Hypochlorite	Electrolysis of salt solution with mixing	—	—	Medium
Iron	Reduction in arc furnace	8–12	—	None
Iron castings	Electric melting			
	Duplex system	0.55	—	Very small
	Continuous	1.78		
Iron, sponge	Electrothermal low-temperature reduction	1.6	—	Very small
Lead	Electrolytic refining	0.7	0.35–0.6	Small
Magnesium, metallic	Electrolysis of magnesium chloride	60–100	6–7	Very large
Phosphoric acid	Electrothermal reduction to phosphorus; oxidation	21	—	Large
Phosphorus	Electrothermal reduction	32–43	—	Large
Potassium hydroxide	Electrolysis of potassium chloride solution	8–9.5	—	Small
Quartz, fused	Electrothermal fusion	40–63	—	Small
Silicon	Electrothermal reduction	48	—	Small
Silicon carbide	Electrothermal reduction	25–30	75–230	Large
Sodium, metallic	Electrolysis of fused sodium chloride	56–58	—	Large
Sodium chlorate	Electrolysis of sodium chloride solution (mixing)	20	2.8–3.5	Small
Steel castings	Electric melting cold charge	2–2.4	—	Large
Steel ingot	Electric melting or refining of molten charge	0.8	—	Large
Zinc	Electrolytic precipitation	11–12	3.5–3.7	Very large

SOURCE: Based on House Doc. 103, 73d Congr.

ALUMINUM

Aluminum is the most abundant metal in the world. It makes up 8% of the solid portion of the earth's crust. Every country possesses large supplies of aluminum-containing materials, but processes for obtaining metallic aluminum from most of these compounds are not yet economical.

HISTORICAL. Aluminum metal was first obtained in pure form in 1825 by Oersted, who heated aluminum chloride with a potassium-mercury amalgam. In 1854, Henri Sainte-Claire Deville produced aluminum from sodium-aluminum chloride by heating with metallic sodium. The process was operated for about 35 years and the metal sold for $220 per kilogram. By 1886 the price had been reduced to $17 per kilogram. In 1886, Charles Hall produced the first aluminum by the present-day large-scale process, electrolysis of alumina in a bath of fused cryolite. The same year, Paul Heroult was granted a French patent for a process similar to that of Hall. By 1893, the production of aluminum had increased so rapidly by Hall's method that the price had fallen to $4.40 per kilogram. The industry grew steadily, based soundly on new and expanding markets created largely by its own study of the properties of aluminum and of the avenues for economical consumption of this new metal. With this growth in manufacture came a decrease in cost which was largely passed on to customers, even reducing the price to 33 cents per kilogram (in 1945). The price has gradually increased and was $1.58 per kilogram in 1980, reflecting inflation and sharp increases in electrical costs. Aluminum is the major nonferrous metal.

ECONOMICS AND USES. The consumption of aluminum is increasing[3] (Table 11.2). Table 11.3 gives the main avenues of distribution. The unusual combination of lightness and strength makes aluminum applicable for many uses that other metals cannot fill. Weight for weight aluminum has twice the conductivity of copper and also has high ductility at elevated

[3]Aluminum Makers Like the Odds, *Chem. Week* 126 (5) 16 (1980).

***Table* 11.2** Primary* Aluminum Production for Selected Years (United States)

Year	Production, kt	Year	Production, kt
1920	63	1974	4457
1930	105	1975	3526
1938	130	1976	3865
1943	836	1977	4126
1952	852	1978	4367
1960	1831	1979	4566
1965	2504	1980	4664
1970	3615	1981	

*Virgin aluminum only; much secondary recovery (around 20 percent of the total) takes place. The United States is usually a net importer of aluminum.

SOURCES: Statistical Committee, *The Aluminum Association Statistical Abstract of the U.S.*, 102 ed.

Table 11.3 U.S. End-Use Distribution of Aluminum (in thousands of metric tons)

End Use	1966	1971	1978	%
Building and construction	902	1258	1292	24
Transportation	887	814	1242	22
Containers and packaging	336	688	1264	23
Electrical	591	649	594	11
Consumer durables	414	440	462	8
Machinery and equipment	297	292	395	7
Exports	265	258	n.a.	
Other	413	331	247	4
Total	4105	4730	5496	99

temperatures. Aluminum is commonly alloyed with other metals, such as copper, magnesium, zinc, silicon, chromium, and manganese, and thus its usefulness is increased. Metallic aluminum or aluminum alloys, particularly with magnesium, are employed in structures for aircraft, automobiles, trucks, and railway cars, for electrical conductors, and for cast and forged structural parts. Properly used,[4] aluminum resists corrosion very well. Its strength and ductility increase at subzero temperatures, which is the opposite of what happens with iron and steel.

MANUFACTURE. Metallic aluminum[5] is produced by the electrolytic reduction of pure alumina[6] in a bath of fused cryolite. For pure alumina, see Chap. 20. It is not possible to reduce alumina with carbon because Al_4C_3 is formed and a back-reaction between aluminum vapor and CO_2 in the condenser quickly reforms the original aluminum oxide again. The enthalpy change involved in the reaction

$$Al_2O_3 + 1\frac{1}{2}C \rightarrow 2Al + 1\frac{1}{2}CO_2 \qquad \Delta H = 1100 \text{ kJ at } 1000°C$$

is equivalent to 20.3 MJ of energy per kilogram of aluminum produced. In actual practice, however, some energy is used to bring reactants up to temperature and some is lost in the sensible heat of the products. Some carbon monoxide is formed in the reaction thus increasing the positive ΔH, which amounts, in practice, to 47.5 to 71.4 MJ/kg. Consequently this metal cannot be made economically unless low-priced electrical energy is available. The carbon for the reduction comes from the anode, which requires from 0.5 to 0.6 kg of carbon per kilogram of metal. Although the theoretical amount required by the equation is 0.33 kg, the carbon dioxide evolved contains from 10 to 50% carbon monoxide, so more is required in practice.

[4]Aluminum for Process Equipment, Part I, *Chem. Eng.* 73 (18) 116 (1966); Part II. *Chem. Eng.* 73 (20) 142 (1966).

[5]For other noncompetitive processes that have been investigated, see ECT, 3d ed., vol. 2, 1978, p. 151; Go Directly to Aluminum, *Chem. Week* 100 (11) 89 (1967); New Processes Promise Lower-Cost Aluminum, *Chem. Eng. News* 51 (9) 11 (1973); Alcoa's Electrolytic Aluminum Process, *Chem. Week* 112 (23) 55 (1973).

[6]PUK Process Separates Aluminum (sic., actually alumina) from Low-Grade Ore, *Chem. Eng. News* 53 (14) 20 (1975).

The steps involved in the production of the metallic aluminum are (Figs. 11.1 to 11.3):

The cell lining is installed or replaced.
Carbon anodes are manufactured and used in the cell.
The cryolite bath is prepared and the composition controlled.
Alumina is dissolved in the molten cryolite bath.
The solution of alumina in fused cryolite is electrolyzed to form metallic aluminum, which serves as the cathode.
The carbon electrode is oxidized by the oxygen liberated.
The molten aluminum is tapped from the cells, alloyed (if desired), cast into ingots, and cooled.

The electrolytic cells are huge boxy steel containers. Inside each is a cathode compartment lined with either a rammed mix of pitch and anthracite coal or coke baked in place by the passage of electric current, or prebaked cathode blocks cemented together. This cathode compartment cavity may be from 30 to 50 cm in depth and up to 3 m wide and 9 m long depending on the type of cell and the load for which it is designed. The cavity-lining thickness varies from 15 to 25 cm on the sides and 26 to 46 cm on the bottom. Thermal insulation consisting of firebrick, asbestos blocks, or other similar materials is placed between the cavity lining and the steel cell. Large steel bars, serving as cathode current collectors, are imbedded in the bottom portion of the cavity lining and extend out through openings in the shell to connect with the cathode bus. Cell linings normally last from 2 to 4 years. When failure occurs, it is usually a result of penetration of metal through to the cathode collectors which it dissolves, or penetration of metal out of the steel shell where it leaks out around the collectors. The entire lining, insulation, and collector ensemble are then replaced. Cell relining is an appreciable part of production expense, including not only the cost of labor, collectors, lining, and insulating materials, but also the loss of electrolyte materials absorbed by the spent lining (producers now reclaim at least some of these electrolyte materials).

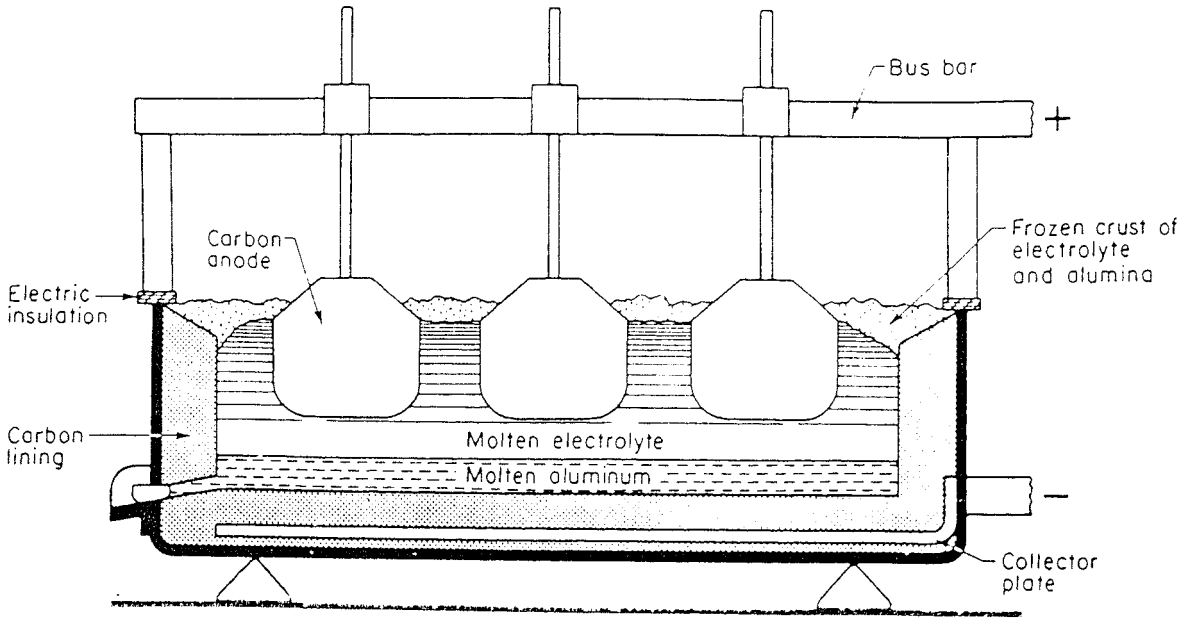


Fig. 11.1. Cross-section diagram of an aluminum reduction pot. *(Aluminum Co. of America.)*

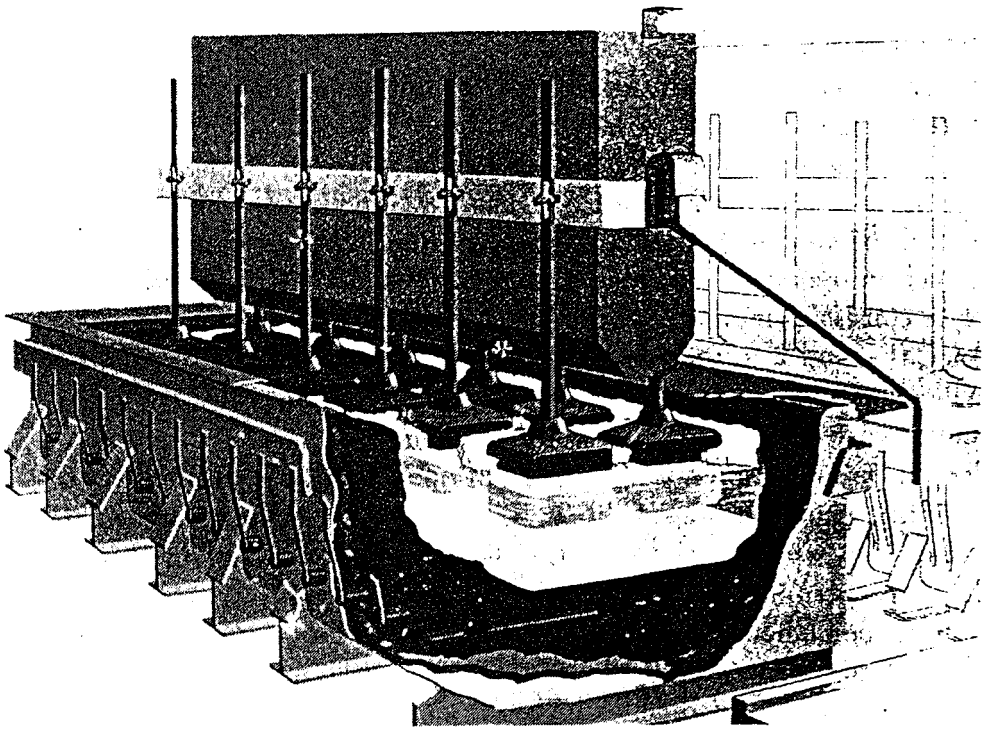


Fig. 11.2. Aluminum reduction pot, showing the actual parts diagrammed in Fig. 14.1 and with the alumina hopper between the carbon anodes. *(Aluminum Co. of America.)*

Two types of cells are used in the Hall-Heroult process, those with multiple prebaked anodes (Figs. 11.1 and 11.2), and those with a self-baking, or Soderberg anode. In both types the anodes are suspended from a superstructure extending over the cell cavity and are connected to a movable anode bus so that their vertical position can be adjusted. The prebaked anode blocks are manufactured from a mixture of low-ash calcined petroleum coke and pitch or tar, formed in hydraulic presses, and baked at up to 1100°C.

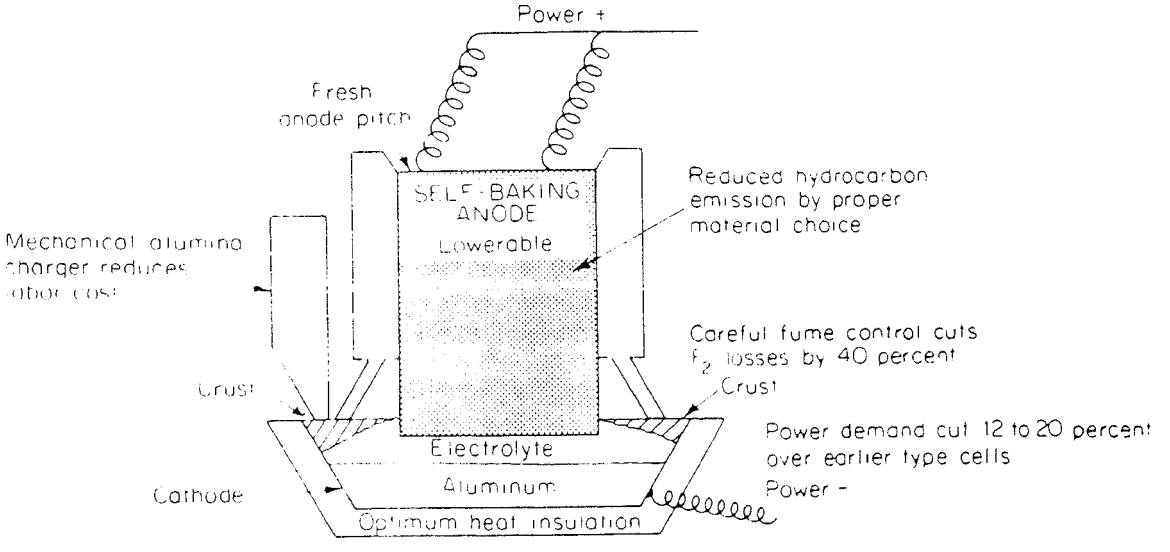


Fig. 11.3. Sumitomo modification of Soderberg cell. Power consumption 50.4 MJ per metric ton of aluminum.

Soderberg[7] anode cells (Fig. 11.3) have a single large anode that subtends most of the cell cavity. The anode is housed in an open steel casing with vertical sides through which it is fed down into the electrolyte. When cells are first placed in operation they are brought up to operating temperature by electric-resistance heating; the anodes are placed in contact with a layer of coke particles on the bottom of the cell cavity and current is passed through the short-circuited cell until the desired temperature is reached. Electrolyte materials are added to the cell cavity around the anode; as these materials gradually become molten, the anodes are raised to put the cell in operation. Normally, the anode-cathode distance is about 5 cm. The molten electrolyte consists principally of cryolite ($3NaF \cdot AlF_3$) plus some excess AlF_3, 6 to 10% by weight of CaF_2, and 2 to 6% Al_2O_3. Some cryolite is imported from Greenland, though most is produced synthetically. AlF_3 is also produced synthetically from hydrogen fluoride and aluminum hydroxide.

The control of electrolyte composition is an important operation in the aluminum production process. As the melting point of pure cryolite is 1009°C, the electrolyte contains fluorspar (CaF_2) and some excess AlF_3 which, along with the dissolved alumina, reduces the melting temperature sufficiently to permit the cells to be operated in the 940 to 980°C range. The excess AlF_3 also improves cell efficiency. The NaF/AlF_3 weight ratio in cryolite is 1.50; the excess AlF_3 in the electrolyte is adjusted to yield an NaF/AlF_3 ratio in the 1.10 to 1.40 range. In the first few weeks after a newly lined cell is placed in operation, the electrolyte is rapidly absorbed into the lining and insulation, with a marked preferential absorption of a high-sodium-containing portion, tending to reduce the NaF/AlF_3 ratio below that desired. Compensation for this is made by adding an alkaline material such as soda ash:

$$3Na_2CO_3 + 4AlF_3 \rightarrow 2(3NaF \cdot AlF_3) + Al_2O_3 + 3CO_2$$

After the first few weeks of operation of the cells, the electrolyte tends to become depleted of AlF_3 through volatilization of AlF_3-rich compounds and through reaction with residual caustic soda in the alumina and hydrolysis from the air or added materials:

$$3Na_2O + 4AlF_3 \rightarrow 2(3NaF \cdot AlF_3) + Al_2O_3$$
$$3H_2O + 2AlF_3 \rightarrow Al_2O_3 + 6HF$$

The volatilized fluorides and gaseous hydrogen fluoride are collected, with other gases evolved from the cells, by gas-collecting hoods or manifolds and are passed through large ducts to central gas-treatment and recovery facilities. Dry scrubbers recover the particulate matter and react the HF with Al_2O_3, which is then fed to the cell. Recovery must be very effective, for small amounts of fluorides in the air severely damage vegetation. Losses from the electrolyte require periodic additions of AlF_3 to maintain the desired composition. The small percentage of lime normally occurring as an impurity in the alumina is sufficient to maintain the desired concentration of fluorspar through the reaction:

$$3CaO + 2AlF_3 \rightarrow 3CaF_2 + Al_2O_3$$

During operation of the cell, a frozen crust forms over the surface of the molten bath. Alumina is added on top of this crust, where it is preheated and has its mechanically absorbed

[7] ECT, 3d ed., vol. 2, 1978, p. 147; Aluminum Cell Modification Cuts Energy Use, *Chem. Eng. News* 53 (31) 19 (1975). Use of Soderberg cells in the United States is diminishing; some turn to prebaking to cut electrode baking cost.

water driven off. The crust is broken periodically, and the alumina stirred into the bath in order to maintain a 2 to 6% concentration. The theoretical requirement is 1.89 kg of alumina per kilogram of aluminum; in practice, the actual figure is approximately 1.91. When the alumina in the bath is depleted, the so-called *anode effect* occurs, wherein a thin film of carbon tetrafluoride forms on the anode so that the bath no longer wets the anode surface, causing an abrupt rise in cell voltage, which is indicated by a signal lamp or bell shunted across the cell and inoperative under normal cell voltage. When this happens, alumina is stirred into the cell, even though the time does not coincide with the routine periodic alumina addition, and the electrolysis process and cell voltage return to normal. The actual mechanism by which alumina is dissolved in the molten bath and electrolytically decomposed is still uncertain. The end results are the release of oxygen at the anode and the deposit of metallic aluminum at the cathode. The oxygen combines with the carbon anode to yield CO and CO_2, with CO_2 predominating.

ALTERNATIVE PROCESSES. Because of the large quantity of electrical power used in the preparation of aluminum, less energy-intensive systems for its preparation are actively being sought, but none is currently in large-scale use. Careful attention to the details of manufacture has reduced the power required by the Hall-Heroult process by 20 percent,[8] but greater reduction is desired. Table 11.4 shows how energy is used for the present process. Recycling used aluminum saves much energy, and this practice is increasing rapidly.[9]

Reduction with carbon (carbothermic), sodium (sodiothermic), manganese (metallothermic), special reactions involving AlF_3 or $AlCl_3$, and electrolysis of $AlCl_3$ (avoiding the costly Bayer refining of bauxite) have been suggested and tested. Carbon reduction is not practical for reasons already stated. Manganese reduction is not sufficiently tested to enable either technical or economic evaluation. Sodium reduction costs far too much.

The chlorine method, involving the following reactions, appeared so promising that a plant, which functioned, was built

$$AlCl_3(g) + 2Al \rightleftarrows 3AlCl(g) \qquad 700\text{–}800°C$$

The reaction volatilized AlCl which was carried out of the reaction zone, then the reaction reversed at lower temperature which freed aluminum. The project proved to be impractical because of difficult corrosion problems. A process showing a 30 percent reduction in power

[8]Weismantel, Needs and Knowhow Boost Aluminum Recycle, *Chem. Eng.* 84 (10) 98 (1977); Rosenzweig, Aluminum Makers Groom New Production Methods, *Chem. Eng.* 82 (15) 62 (1975).

[9]Deutsch, Aluminum: Energy Diet Pays Off, *Chem. Eng.* 86 (23) 94 (1979).

***Table* 11.4** Energy Required to Produce a Metric Ton of Aluminum

Operation	Thermal Energy Required, MJ	Electrical Energy Required, MJ	Total MJ
Mining and refining	30,000	5,200	35,200
Winning	27,000	158,900	185,900
Mill processing	30,000	17,700	47,700
Total	87,000	181,800	268,800

over the best Hall-Heroult cells is operated on a modest scale by Alcoa. It utilizes a closed system and the reactions:

$$2Al_2O_3 + 3C + 6Cl_2 \rightarrow 4AlCl_3 + 3CO_2$$

$$2AlCl_3 \xrightarrow{\text{electrolysis}} 2Al + 3Cl_2$$

Deposits of high-grade bauxite are rapidly being used up, and almost all are outside the United States. Attention is, therefore, being given to other possible sources. There is no lack of such sources,[10] but the problem is economical extraction of sufficiently pure alumina. Table 14.5 shows the availability and size of alternate aluminum sources.

MAGNESIUM

Magnesium is a very light, silvery-white metal that has achieved considerable industrial use. Magnesium is the eighth most abundant element in the world. The raw materials are widely distributed throughout the globe, particularly since seawater is a practical and very important source of magnesium compounds. Major ores are dolomite ($CaCO_3 \cdot MgCO_3$), magnesite ($MgCO_3$), and carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$). A cubic kilometer of seawater contains 1.3×10^6 t of magnesium, making the sea a resource of 1.7×10^{24} t, a staggering amount. There need never be any shortage of the economical raw materials for magnesium metal and its salts. Magnesium salts are considered in Chap. 10.

HISTORICAL. Although metallic magnesium was first isolated by Bussy in 1829, its existence was discovered by Davy in 1808. As late as 1918, almost all the magnesium produced was used for photographic flash powder and in pyrotechnics. The U.S. output in 1918 was only 129,144 kg. Intensive research brought forth many new uses for magnesium. By 1930 it was being fabricated into complicated castings, sheets, and forgings, and a method of welding it was also perfected. Extremely strong, lightweight magnesium alloys[11] of great importance to

[10]Felker, Seeley, Egan, and Kelmers, Aluminum from Fly Ash, *CHEMTECH* 12 (2) 123 (1982).

[11]Comstock, *Magnesium and Magnesium Compounds*, U.S. Bureau of Mines Inf. Circ. 8201, 1963; Hanawalt, "Magnesium Industry," World Magnesium Conference, Montreal, October 1963; Steady Growth Forecast for Magnesium Use, *Chem. Eng. News* 57 (30) 15 (1979); Deutsch, Magnesium's Hopes Grow—but So Do Reduction Costs, *Chem. Eng.* 57 (13) 116 (1979).

***Table* 11.5** Potential Sources of U.S. Aluminum

Mineral	Resource, 10^6 t
Bauxite, $Al_2O_3 \cdot 2H_2O$	33
Kaolin, $xAl_2O_3 \cdot ySiO_2 \cdot 2H_2O$	290
Clays	690
Shale	58
Alunite, $K_2Al_6(OH)_{12}(SO_4)_4$	29
Dawsonite, $Al_2(CO_3)_2 \cdot Na_2CO_3 \cdot nH_2O$	3,000
Anorthosite, $(Na,Ca)Al(Si,Al)Si_2O_8$	13,600
Coal refuse	3,000

the aircraft industry were developed and met demands during World War II and after. Magnesium production expanded tremendously. Common magnesium alloys are AZ91B: Al 6.5%, Mn 0.2%, Zn 3%, and the rest magnesium for pressure die casting; and AZ31: Mn 1.5% and the rest magnesium for wrought products.

USES AND ECONOMICS. The largest single use of magnesium, the world's lightest structural metal, is in aluminum alloying, for use in such varied places as space vehicles and automotive parts. Other uses include preparation of the Grignard reagent, pyrotechnics and explosives, sacrificial anodes to prevent corrosion, lightweight housings for power tools and automobiles, and as a reducing agent in producing titanium, zirconium, uranium, and beryllium. During World War II, primary magnesium production averaged over 96,000 t yearly; it then dropped to about 9100 t annually, but has increased steadily since: 1974—72,000, 1976—109,052, 1980—154,425 t. Four companies produced primary magnesium in the United States in 1980, with Dow the major producer. Secondary magnesium, recovered at a great saving of power, represented 20 percent of the total 1980 production. As usual in the development of a material from a rarity to major tonnage, the price of magnesium fell from $4.00 per kilogram in 1918 to 78 cents per kilogram in 1970, although it has since risen to $2.55 per kilogram. Much magnesium is recovered from scrap (7817 t in 1977). Since it requires 170 MJ/kg to produce primary magnesium but only 6.7 MJ/kg if made from recycle, the recovery is very desirable.

MANUFACTURE. The cheapest method of making magnesium is by the electrolytic process. During World War II magnesium was made by two other processes, the silicothermic, or ferrosilicon process and the carbon reduction process. The carbon reduction process[12] never operated satisfactorily, and its use has long been discontinued. The silicothermic process is still used in areas where power is expensive and only small magnesium capacity is required (Fig. 11.4).

Electrolysis of Magnesium Chloride. The magnesium chloride[13] needed is obtained (1) from salines, (2) from brine wells, and (3) from the reaction of magnesium hydroxide (from seawater or dolomite) with hydrochloric acid (Fig. 11.5). The pioneer producer, Dow Chemical Co. at Freeport and Velasco, Tex., makes magnesium by electrolyzing magnesium chloride from seawater, using oyster shells for the lime needed. The oyster shells, which are almost pure calcium carbonate, are burned to lime, slaked, and mixed with the seawater, thus precipitating magnesium hydroxide (Fig. 11.5). This magnesium hydroxide is filtered off and treated with hydrochloric acid prepared from the chlorine evolved by the cells. This forms a magnesium chloride solution that is evaporated to solid magnesium chloride in direct-fired evaporators, followed by shelf drying. The chloride tends to decompose on drying. After dehydrating, the magnesium chloride[14] is fed to the electrolytic cells, where it is decomposed into the metal and chlorine gas. These cells are large rectangular ceramic-covered steel pots, 1.5 m wide, 3.3 m long, and 1.8 m deep, with a capacity of about 9 t of molten magnesium chloride and salts. The internal parts of the cell act as the cathode, and 22 graphite anodes

[12]For description and references see CPI 1, pp. 310–311.

[13]Shigley, Minerals from the Sea, *J. Metall.* **191** (1) 25 (1951); Davis, Magnesium, Maybe This Time, *Chem. Eng.* 80 (19) 84 (1973); Magnesium Cast for New Roles, *Chem. Week* 112 (3) 24 (1973).

[14]Teaming Up to Tap Brines, *Chem. Week* 98 (8) 15 (1966); Magnesium Makes Its Move, *Chem. Eng.* 76 (18) 60 (1969); Anderson, World's Nations Scramble for Sea's Riches, *Chem Eng. News* 52 (9) 18 (1974).

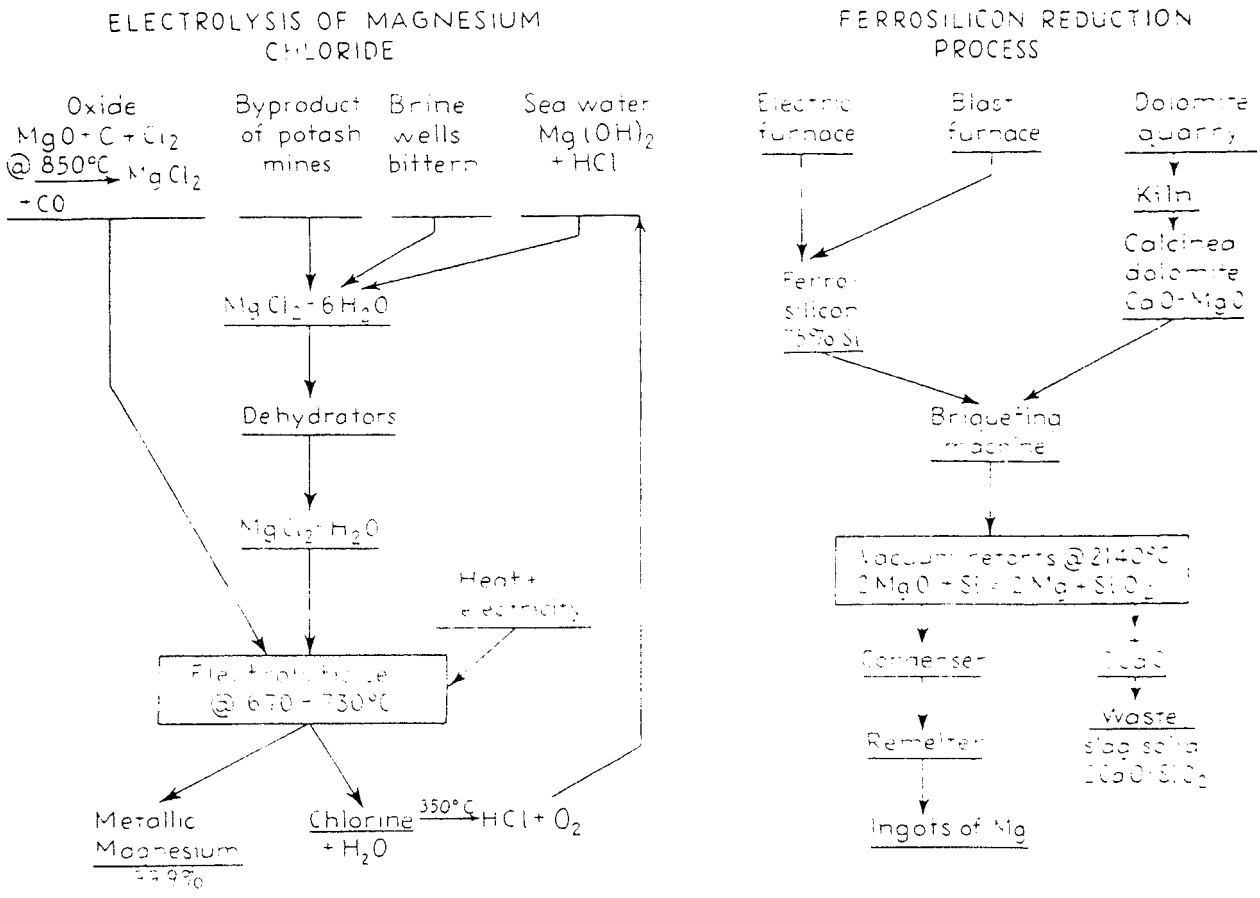


Fig. 11.4. Outline of alternate processes for the production of metallic magnesium

are suspended vertically from the top of the cell. The arrangement is very similar to the Downs sodium cell (Fig. 11.6). Sodium chloride is added to the bath to lower the melting point and also increase the conductivity. The salts are kept molten by the electric current used to extract the magnesium plus external heat supplied by external gas-fired furnaces. The usual operating temperature is 710°C, which is sufficient to melt the magnesium (mp 651°C). Each cell operates at about 6 V and 80,000 to 100,000 A, with a current efficiency above 80 percent. The power requirements are 63.4 MJ/kg of magnesium produced. The molten magnesium is liberated at the cathode and rises to the bath surface, where troughs lead to the metal wells in front of the cell. The 99.9% pure magnesium metal is dipped out several times during the day, each dipperful containing enough metal to fill a 20-kg self-pelleting mold.

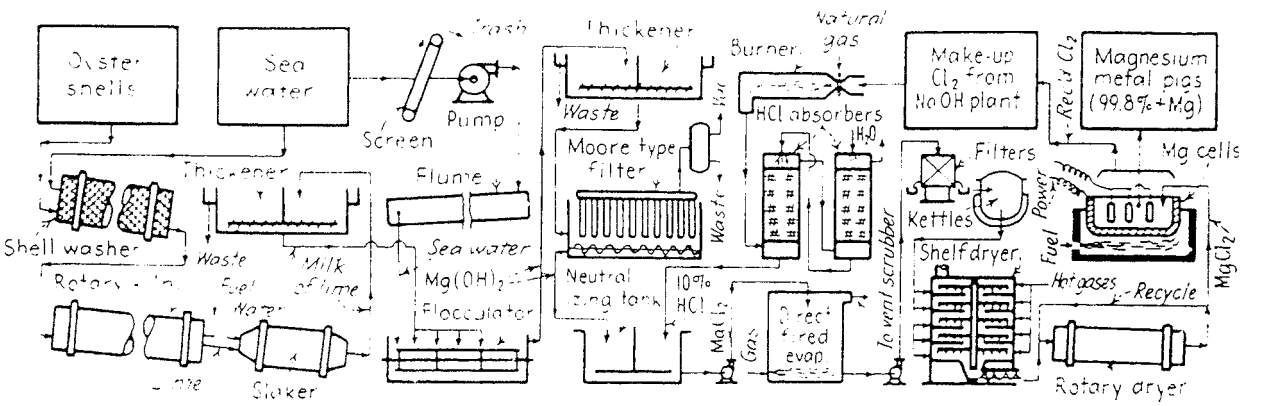


Fig. 11.5. Magnesium metal from seawater—Dow process

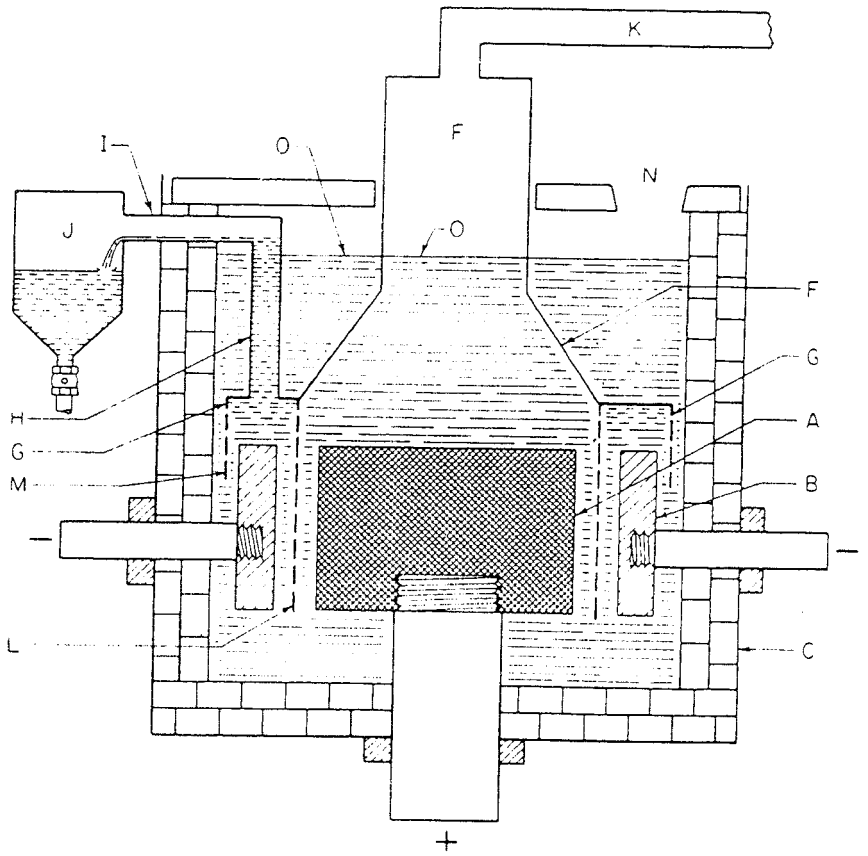


Fig. 11.6. Downs sodium cell. (A) Graphite anode; (B) iron cathode; (F) dome for collecting the chlorine; (K) pipe for conducting the chlorine away; (G) annular sodium collector; (H) and (I) pipes to conduct the sodium to the vessel (J); (L) and (M) metal screens supported by (F) and serving to separate the cell products; (C) shell of the cell made of steel but lined with refractory bricks; (N) charge port for salt; and (O) bath level.

Silicothermic, or Ferrosilicon, Process.[15] During World War II, the U.S. government financed construction of six silicothermic plants (Fig. 11.4) with a total rated capacity of 64,000 t/year, which were eventually dismantled. Later, private interests constructed silicothermic plants at Selma, Ala. and Addy, Wash. The essential reaction of this process is:

$$2(MgO \cdot CaO) + \tfrac{1}{6}FeSi_6 \rightarrow 2Mg + (CaO)_2SiO_2 + \tfrac{1}{6}Fe$$

The process consists of mixing ground, dead-burned dolomite with ground 70 to 80% ferrosilicon and 1% fluorspar (eutectic) and pelleting. The pellets are charged into the furnace. High vacuum and heat (1170°C) are applied. The calcium oxide present in the burnt dolomite forms infusible dicalcium silicate that is removed from the retort at the end of the run. A variant of the process (magnathermic system) adds sufficient Al_2O_3 to produce a liquid slag; operation is at a higher temperature (1600°C). The chrome-alloy retort is equipped with a condenser tube with a removable liner. The reaction is run at very high vacuum (13 to 20 Pa), and the liberated magnesium is collected on the lining of the condenser. At the end of the run, the furnace is partly cooled, and the magnesium is removed from the condenser by a procedure based on the difference in contraction of magnesium and steel, and taken to the remelt furnace. This process is not currently competitive.

[15]Schrier, Silicothermic Magnesium Comes Back, *Chem. Eng.* 59 (4) 148 (1952).

SODIUM[16]

Sodium is a silvery white, very active metal. It reacts violently with water and is usually preserved in containers under a nitrogen blanket or, less satisfactorily, under dry, liquid kerosene. About 60,000 t of sodium enters annually into the manufacture of tetraethyl- and tetramethyllead, and the rest is used for metals reduction (particularly of titanium), Na_2O_2, metal descaling, dyes, pharmaceuticals, and herbicides. The total U.S. consumption in 1981 was 102,000 t.

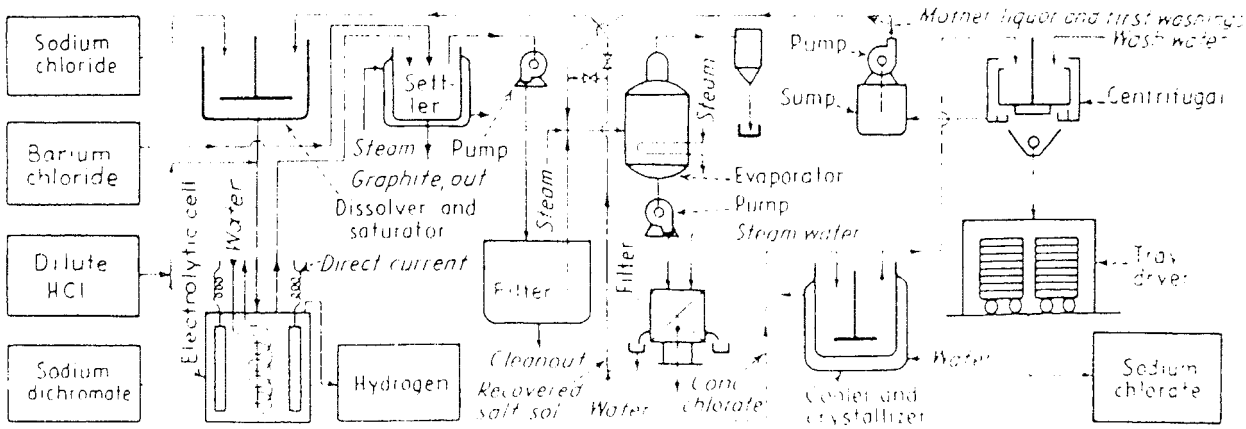
MANUFACTURE. The most important method of preparation of sodium is by the electrolysis of fused sodium chloride. The reaction involved is

$$2NaCl \rightarrow 2Na + Cl_2$$

The cell for this electrolysis consists of a closed, rectangular, refractory-lined steel box (Fig. 14.6). The anode is made of carbon and the cathode of iron.[17] The anode and cathode are arranged in separate compartments to facilitate the recovery of the sodium and the chlorine. Sodium chloride has a high melting point (804°C), but calcium chloride is added to lower it, and the cell is operated at 600°C. The electrolyte is a eutectic of 33.2% sodium chloride and 66.8% calcium chloride. The lower temperature increases the life of the refractory lining of the cell, makes it easier to collect the chlorine, and prevents the sodium from forming a fog that is difficult to recover. A sodium-calcium mixture collects at the cathode, but the solubility of calcium in sodium decreases with decreasing temperatures so that the heavier calcium

[16]*Sodium-NaK Engineering Handbook*, Gordon and Breach, New York, 1972.

[17]Downs, Electrolytic Process and Cell, U.S. Patent 1,501,756 (1924); Zabel, Metallic Sodium, *Chem. Ind.* 65, 714 (1949).



In order to produce 1 t of sodium chlorate, the following materials and utilities are required.

Salt (sodium chloride)	514 kg	Electric power, dc	18,400 MJ
Hydrochloric acid	12.8 kg	Steam	5 t
Sodium dichromate	0.45 kg	Motor requirements	228 MJ
Barium chloride	5.9 kg	Water (25°C)	22 t
Graphite consumed	[illegible] kg	Labor	8 work-h

Fig. 11.7 Flowchart for the manufacture of sodium chlorate.

crystals, which form as the mixture is cooled, settle back into the bath. The crude sodium is filtered at 105 to 110°C, giving a sodium purity of 99.9%. This is run molten into a nitrogen-filled tank car, allowed to solidify, and shipped.

CHLORATES AND PERCHLORATES[18]

Sodium chlorate is manufactured in large quantities (about 258,000 t in 1981). About half of the production is used for bleaching pulp, with solid rocket propellants (through ammonium perchlorate), herbicides, defoliants, and potassium perchlorate for explosives using up most of the remainder.

MANUFACTURE. *Sodium chlorate* is produced by the electrolysis of saturated, acidulated brine mixed with sodium dichromate (about 2 g/L) to reduce the corrosive action of the hypochlorous acid present. Figure 11.7 shows the essential steps in the production of this chemical. The brine solution is made from soft water or condensate from the evaporator and rock salt purified of calcium and magnesium. The rectangular steel cell is filled with either the brine solution or a recovered salt solution, made from recovered salt-containing chlorate, dissolved in condensate from the evaporator. Electrodes are graphite and steel for small cells, graphite and graphite for larger cells and, in new cell designs, dimensionally stable (DSA) anodes of coated titanium. Anodes of tantalum and niobium are also being tested. Improved anodes result in high cell efficiencies and much higher current densities. The temperature of the cell is maintained at 40°C (higher when DSA anodes are used) by cooling water. The products of the electrolysis are actually sodium hydroxide at the cathode and chlorine at the anode, but since there is no diaphragm in the cell, mixing occurs and sodium hypochlorite is formed, which is then oxidized to chlorate. The overall reaction is:

$$NaCl(aq) + 3H_2O(l) \rightarrow NaClO_3(aq) + 3H_2(g) \qquad \Delta H = 937 \text{ kJ}$$

The finished cell liquor is pumped to tanks where it is heated with live steam to 90°C to destroy any hypochlorite present. The liquor is analyzed to determine the chromate content, and the required amount of barium chloride is introduced to precipitate almost all the chromate present. The graphite mud from the electrodes and the barium chromate settle to the bottom of the tank, and the clear liquor is pumped through a filter to the evaporator storage tanks. The liquor in the storage tank is neutralized with soda ash and evaporated in a double-effect evaporator until it contains approximately 750 g/L of sodium chlorate. After evaporation, the liquor is allowed to settle to remove the sodium chloride, which constitutes the recovered salt and chlorate, to be used over again. The settled liquid is filtered and cooled. The crystals of sodium chlorate which drop out are spun in a centrifuge and dried.

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[18]Schumacher, *Perchlorates*, ACS Monograph, Reinhold, New York, 1960; ECT 3d ed. vol 5, 1979, p. 633; Reynolds and Clapper, The Manufacture of Perchlorates, *Chem. Eng. Prog.* **57** (11) 138 (1961); Remirez, Producing Captive Sodium Chlorate in Integrated Pulp Mills, *Chem. Eng.* **74** (17) 136 (1967)

Potassium perchlorate is made by converting sodium chlorate into sodium perchlorate in steel electrolytic cells, which have platinum anodes and operate at 5.5 to 6.0 V, 2500 A, and a temperature of 65°C. Filtered potassium chloride solution is added to the sodium perchlorate, precipitating potassium perchlorate crystals, which are centrifuged, washed, and dried. The mother liquor now contains sodium chloride, which can be used as a cell feed for sodium chlorate manufacture. Perchlorate may also be manufactured by electrolysis of potassium chloride solutions.

Potassium chlorate is used in matches, pharmaceutical products, and pyrotechnic mixtures. Most mixtures of organic substances and chlorates are explosive so use of any such mixtures should be limited to those expert in their use.

OTHER PRODUCTS

Elsewhere in this book a few electrolytic processes are presented, as in the special chapter (Chap. 10) pertaining to caustic soda and chlorine. Electrolytic hydrogen and oxygen are included with the other procedures for hydrogen in Chap. 4 on industrial gases. Mention is made of electrolytic fluorine in Chap. 20. In Germany, HCl is electrolyzed to chlorine and hydrogen at 66°C.[18a]

ORGANIC COMPOUNDS[19]

As the science of electroorganic chemistry has been put on a firmer footing, the technology has begun to take root and shows signs of major expansion. Electricity is expensive as energy, but relatively inexpensive when considered as a reagent. Several electroorganic processes have been tried and later abandoned when less expensive chemical or biological routes have been discovered. Sorbitol, mannitol, and gluconic acid and its salts have been made by the electrooxidation of glucose. The major large-scale operation in current use is the conversion of acrylonitrile to adiponitrile; Monsanto[20] operates a very large plant.

Other plants either operated on a small scale or being tested abroad include phthalic acid to dihydrophthalic acid, acetone to pinacol, monomethyladipate to dimethyl sebacate, perfluorination of various amines and organic acids, some less than perfluorinated derivatives, and tetraethyl lead.

[18a]Chlorine: New Process, *Chem. Eng.* 72 (3) 62 (1965).

[19]Eberson and Weinberg, Electroorganic Synthesis, *Chem. Eng. News* 49 (4) 40 (1971); Fitzjohn, Electro-organic Synthesis, *Chem. Eng. Prog.* 71 (2) 85 (1975); Dotson, Modern Electrochemical Technology, *Chem. Eng.* 85 (16) 106 (1978); Organic Electrochemistry Making Big Strides, *Chem. Eng. News* 56 (10) 20 (1978).

[20]Prescott, Monsanto's Unique Process, *Chem. Eng.* 72 (23) 238 (1965); Baizer, The Electrochemical Route to Adiponitrile, I—Discovery, *CHEMTECH* 10 (3) 161 (1980); Danley, The Electrochemical Route to Adiponitrile, II, *CHEMTECH* 10 (5) 302 (1980).

PRIMARY AND SECONDARY CELLS[21]

Chemical reactions can be used to convert chemical energy to electrical energy, which is the converse of the procedures presented in the earlier parts of this chapter. The chemical reaction can be caused to take place in a unit especially designed for the purpose of obtaining electrical energy. These units are commonly called cells, or batteries. *Primary cells* produce electricity by means of a chemical reaction that is not readily reversible, so the chemicals must be replaced after the reaction has taken place. *Secondary cells* depend upon chemical reactions that are reversible by electrical energy and therefore do not require replacement of the chemical components. The cost of electrical energy from primary batteries is very high, especially if they are used to produce large quantities of electricity. Battery sales totaled $3300 million in 1979, of which at least $600 million was for ingredient chemicals, including metals.

Development of low-weight high-power-content secondary cells could revolutionize energy use by leveling out the load factor of power plants, making electrically powered vehicles satisfactory for general use, and perhaps making wind and tidal power economically possible.

The common dry cell is a very old device, the direct descendant of the Leclanche cell. The cathode current collector is a carbon rod, the anode is zinc, the electrolyte is zinc chloride or zinc chloride–ammonium chloride mixture made into a paste with a gelling substance (starch and flour have been used) with manganese dioxide present as a depolarizer. A cardboard and plastic container surrounds and insulates this "dry" cell.

Fuel cells are primary cells using catalyzed combustion processes to generate electricity. Where reliability, low weight per unit of power produced, and an indifference to cost prevail, they are excellent. They are also the units that show the most promise for large-scale, efficient generation. Substantial installations that will quietly generate energy for household use and that have few moving parts are now being built. Because of their quiet and nonpolluting characteristics, they can be placed close to the consumer, saving distribution cost. (See Chap. 4 for theory and discussion.) Fuels used include reformed hydrocarbons, methanol, ammonia, hydrazine, and hydrogen with air or oxygen, the usual oxidizer.

The most important secondary cell is the *lead storage battery*. The reactions that take place on discharge between two electrodes dipping into partly diluted sulfuric acid are

At positive lead peroxide plate (cathode)

$$PbO_2(s) + 4H^+(aq) + 2e \rightarrow Pb^{2+}(aq) + 2H_2O(l)$$

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$$

$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

[21]ECT, 3d ed., vol. 3, 1978, p. 503; Packing More Punch into Electric Batteries, *Chem. Eng.* **74** (2) 90 (1967); Ramirez, Battery Development Revs Up, *Chem. Eng. News* **86** (18), 49 (1979); New Batteries Are in the Running, *Chem. Week* **119** (22), 31 (1976); Battery Development Makes Good Progress, *Chem. Eng. News* **55** (8) 28 (1977); New Materials Boost Battery Research, *Chem. Eng. News* **56** (40) 14 (1978).

AT NEGATIVE SPONGE LEAD PLATE (ANODE)

$$\begin{aligned} Pb(s) &\rightarrow Pb^{2+}(aq) + 2e \\ Pb^{2+}(aq) + SO_4^{2-}(aq) &\rightarrow PbSO_4(s) \\ \hline Pb(s) + SO_4^{2-}(aq) &\rightarrow PbSO_4(s) + 2e \end{aligned}$$

OVERALL REACTION

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O$$

Electrical energy is generated when these reactions take place. To restore the activity, that is, recharge the battery, electrical energy is applied and the reactions are reversed. The battery consists of lead plates in the form of a grid filled, when charged, with lead peroxide at the positive plate and sponge lead at the negative plate. The plates are insulated from each other by means of separators made of microporous materials: ploy vinyl chloride, polyester, polypropylene, rubber, or glass. The battery is filled with diluted sulfuric acid. An ordinary battery consists of 13 to 15 plates per cell and has several cells in series. It delivers 2 V per cell.

Another widely used secondary cell is the *Edison battery*. The positive plate consists of nickel peroxide and flaked metallic nickel; the negative plate is finely divided iron. The electrolyte consists of a mixture of potassium hydroxide and lithium hydroxide. The battery finds widest use in heavy-duty industrial and railway applications.

The *nickel-cadmium*[22] secondary cell resembles the Edison nickel-iron cell, but it has better storage life, losing only about 10 percent of capacity in the first 48 h and then about 3 percent or less per month. This cell employs nickel hydroxide and cadmium–cadmium hydroxide as the electrochemically active materials of the positive and negative electrodes, respectively. The electrolyte is an aqueous solution of potassium hydroxide. The overall cell reaction may be approximately represented as:

$$\underset{\text{Charged}}{2Ni(OH)_3} + Cd \rightarrow \underset{\text{Discharged}}{2Ni(OH)_2} + Cd(OH)_2$$

Nominal discharge voltage is about 1¼ V per cell. These cells are rugged, low-gassing, efficient at low temperatures, and, though more expensive, are employed for important stand-by and emergency service, portable service, and for cordless appliances such as shavers and toothbrushes. The Telstar satellite had a communication system powered by 19 nickel-cadmium batteries.

Battery development is being vigorously pursued and promising leads are developing. Table 14.6 shows some obtainable characteristics of less common battery combinations compared with the best available lead-acid units. The figures should be viewed with caution, since current developments are causing them to change rapidly. For an automobile to have a 100-mile range at a reasonable speed without recharge, an energy density of 356 kJ/kg with a total capacity of 178,000 kJ is required with modestly low cost. This goal is at present unobtainable.

An interesting new development gives promise of real advancement in the field, although

[22]Booster for Battery Chemicals, *Chem. Week* **101** (13) 111 (1962).

***Table* 11.6** Characteristics of Rechargeable Battery Systems

	Cell Energy Density, kJ/kg	Operating Temperature, C°	Cell Life, Times Rechargable
Lead-acid	160–200	20–30	1000
Lithium-iron sulfide	630–670	380–450	1000
Sodium-antimony trichloride	400	200	175
Sodium-sulfur	555	250–300	400
Nickel-zinc	240	20–30	250
Nickel-iron (Edison)	160	20–30	3000
Zinc-chlorine	200	50	100

neither the technology nor the costs have been worked out. Organic batteries[23] using no metal in their construction having polyacetylene or poly(*p*-phenylene) electrodes and tetrabutylammonium perchlorate in propylene carbonate electrolyte have good energy density and give very large currents for their size.

Batteries using biological processes are also under study

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[23]Dagani, Organic Battery Uses Polyacetylene Electrodes, *Chem. Eng. News* 59 (4) 39 (1981); Dagani, Polymer Cells Offer More Power, Less Weight, *Chem. Eng. News* 59 (41) 34 (1981); Douglas and Kirk, Batteries for Energy Storage, Parts I and II, *CHEMTECH*, 13 (1) 58 (1983); 13 (2) 120 (1983)

Chapter 12

Electrothermal Industries

Many chemical products made at high temperatures demand the use of an electric furnace. Electric furnaces are capable of producing temperatures as high as 4100°C. This may be contrasted with the highest commercial combustion-furnace temperatures of about 1700°C. The effects of high temperature are twofold: The *speed* of the reaction is *increased*, and *new conditions* or *equilibrium* are established. These new equilibrium conditions have resulted in the production of compounds unknown before the electric furnace. Silicon and calcium carbides are examples of new products thus formed. The electric furnace affords more exact control and more concentration of heat with less thermal loss than is possible with other types of furnaces. This favorable situation is caused by the lack of flue gases and by the high temperature gradient between the source of heat and the heated mass. The electric furnace is much cleaner and more convenient to operate than the combustion furnace. It is operated by alternating current of high amperage, usually with moderate voltage, whereas the electrolytic industries require direct current.

The chief types of electric furnaces[1] are arc, induction, resistance, and plasma. The heat in the arc furnace is produced by an electric arc between two or more electrodes, which are usually graphite or carbon, between the electrodes and the furnace charge, or between two or more electrodes, which are usually graphite or carbon and may or may not be consumed in the operation, or between the electrodes and the furnace charge. The furnace itself is generally a cylindrical shell lined with a refractory material. Its use is not limited to those industries for which it is a necessity; some companies have rolling-mill operations for common quality steels where electric-arc furnaces are the sole source of ingots.

Almost 20 percent of the steel produced worldwide is now made in electric arc and induction furnaces. Ferro-alloys are also produced in arc and induction furnaces. These operations are usually operated batchwise. Submerged arc shaft furnaces operate with continuous feeding of solids at the top and periodic tapping of the molten phases which collect at the base. They are used for the production of elemental phosphorus and calcium carbide.

The induction furnace may be applied only for conducting substances such as metals, where the electrical energy is converted into heat by induced currents set up in the charge. The furnace can be considered as a transformer, with the secondary consisting of the metallic charge and the primary of heavy copper coils connected to the power source. Induction fur-

[1]Mantell, *Electrochemical Engineering*, 4th ed., McGraw-Hill, New York, 1960; Hamblyn, Plasma Technology and Its Application to Extractive Metallurgy, *Miner. Sci. Eng.* 9 (3): 151 (1977); Fitzgerald, Arc Furnace Steelmaking, *IESM* 9 (1): 24 (1982).

naces operate at frequencies from 60 to 500,000 Hz, but those used in commercial-scale electrothermal processes do not usually use frequencies above 6000 Hz. The heating effect is obtained with lower field strengths as the frequency is increased. The charge should be placed around an iron core in the low-frequency furnace, but this core is unnecessary for high-frequency furnaces. When the charged material furnishes the electric resistance required for the necessary heat, the furnace is *direct-heated* resistance; when high-resistance material is added to the charge for the purpose of creating heat, the furnace is *indirect-heated*. Batch-operated resistance furnaces are used for the production of silicon carbide and graphite electrodes. Continuous vertical shaft resistance furnaces are used for the calcination of anthracite to produce conductive carbon for aluminum cell cathode construction. In the electrochemical industry, the arc and the resistance furnaces are most used.

A plasma arc furnace is an electrically heated gas furnace which produces a high temperature (3730 to 4730°C). Almost any gas can be used. The gas is passed through an electric arc that burns continuously between two electrodes and is partially ionized. The hot ionized gas (plasma) is then introduced into the reaction chamber. This system has been proposed for the reduction of iron ore, but few commercial applications have been made because of its high cost. However, the increased emphasis on environmental control and occupational safety are making the cost factor less important. A plant to produce ferrochrome with a plasma smelter is being constructed in South Africa.

ARTIFICIAL ABRASIVES

HISTORICAL. Before 1891 all abrasives used were natural products such as diamonds, corundum, emery, garnet, quartz, kieselguhr, and rouge. In that year E. G. Acheson produced the first synthetic abrasive in a homemade electric-arc furnace while attempting to harden clay. Acheson found these new hard purple crystals to be silicon carbide. Discovering that these crystals were hard enough to cut glass, he sold them, under the trade name Carborundum, to gem polishers for $1940 per kilogram.[2] Another make of silicon carbide is sold under the tradename Crystolon. Fused aluminum oxide, the most extensively used abrasive, is manufactured in an electrothermal furnace. Boron nitride, or Borazon, one of the hardest substances made synthetically, is an electrothermal product.

USES AND ECONOMICS. The discovery and production of artificial abrasives marked the beginning of the evolution of modern grinding tools, which are of paramount importance in the modern precise fabrication of multitudinous metal parts for automobiles, airplanes, machines, dies, and other manufactured items of present-day industrial endeavor. To reduce wear, harder and harder alloys are being developed by the metallurgist, many of which can be finally shaped economically only by these hard artificial abrasives. Silicon carbide and alumina are also used as a refractory material, both in the form of brick and as loose material for ramming in place. Between 30 and 50 percent of silicon carbide production is used for an additive in the manufacture of iron and steel. Refractory and metallurgical uses now consume about 70 percent of the silicon carbide produced, and the traditional use as an abrasive

[2]Cooper, Modern Abrasives, *J. Chem. Educ.* 19 122 (1942); Upper, The Manufacture of Abrasives, *J. Chem. Educ.* 26 676 (1949).

consumes a minor part of the production. In the U.S. and Canada, the production of silicon carbide exceeds 225,000 t,[2a] and that of fused aluminum is about 180,000 t/year. Impermeable silicon carbide[3] withstands 1000°C and resists corrosion, erosion, and coerosion.

SILICON CARBIDE. The raw materials for the production of silicon carbide[4] are sand and carbon. Carbon is obtained from petroleum cokes, and sand contains 98 to 99.5% silica. The equations usually given for the reactions involved are

$$SiO_2(c) + 2C(amorph) \rightarrow Si(c) + 2CO(g) \qquad \Delta H = +606 \text{ kJ}$$
$$Si(c) + C(amorph) \rightarrow SiC(c) \qquad \Delta H = -127.7 \text{ kJ}$$

The total reaction obtained by combining these equations is

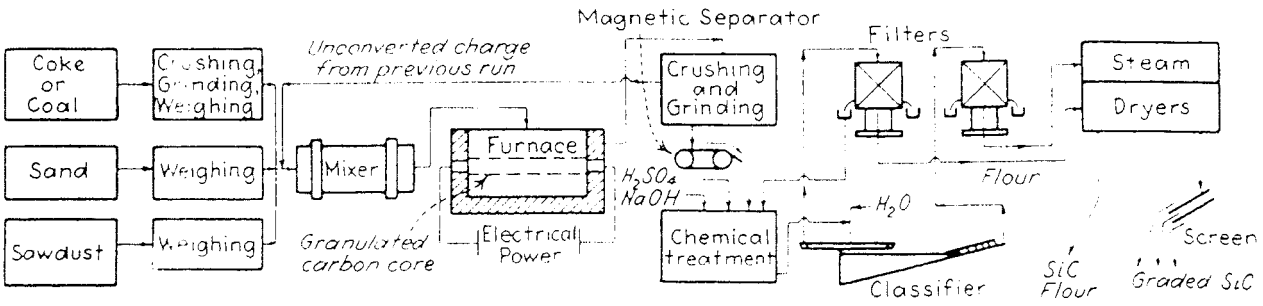
$$SiO_2(c) + 3C(amorph) \rightarrow SiC(c) + 2CO(g) \qquad \Delta H = +478.3 \text{ kJ}$$

Figure 12.1 is a flowchart for the production of silicon carbide. Figure 12.2 shows the furnace itself. Sand and carbon are mixed in an approximate molar ratio of 1:3 and charged into the furnace. Sawdust, if added, increases the porosity of the charge and permits the circulation of vapors and the escape of the carbon monoxide produced. The furnace is a trough 12 to 24 m long, 3 m or more wide, and 2 to 3 m high. The ends of the trough are the electrodes, which are connected to a central heating core of graphite. The walls of the furnace are loose refractory bricks, which are held in place by a steel frame. Excessive heat loss does not occur because the outside unreacted charge serves as an insulator. As the silicon carbide is formed, the conductivity of the charge increases and the power is adjusted by lowering the voltage. A typical initial current between the electrodes is 6000 A at 230 V, and the final current may be 20,000 A at 75 V. Initially, the core heats up to 2040°C but then the temperature gradually falls to 1600°C. The outer edges of the furnace remain at about

[2a]t = 1000 kg.

[3]Roe and Kwasniewski, Resist Wear and Acids with Silicon Carbide, *Chem. Eng. Prog.* 60 (12) 97 (1964); McManus, Steelmakers Searching for Refractories That'll Take the Heat, *Iron Age* 223 (40) MP-7 (1980).

[4]ECT, 3d ed., vol. 4, 1978, p. 520; New Silicon Carbide Process Being Tested, *Chem. Eng. News* 59 (29) 28 (1981).



In order to produce 1 t of finished silicon carbide (including unconverted charge), the following materials and utilities are needed:

Sand	2.10 t	Sawdust (if used)	0.5 t
Coke	1.40 t	Electricity	28–33 MJ

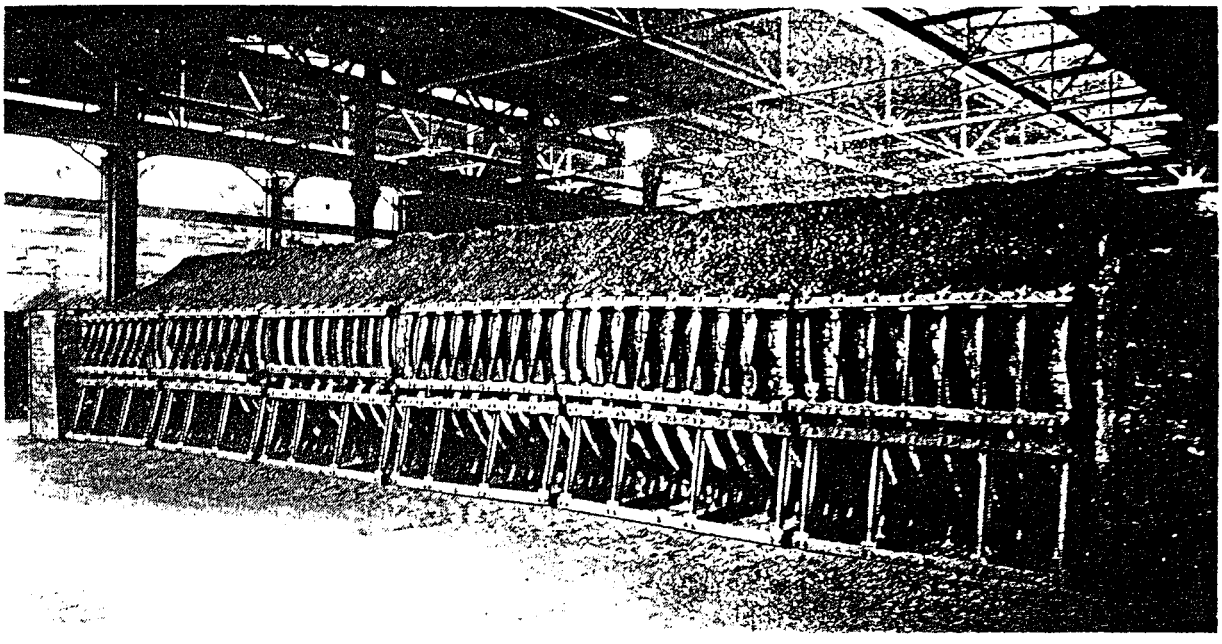


Fig. 12.2. Electric resistance furnace in which Carborundum brand silicon carbide is produced. (*The Carborundum Co.*)

1370°C. The temperature should not become too high, or the silicon carbide will decompose with the volatilization of silicon and the formation of graphite. Indeed, artificial graphite was so discovered.

The time of the reaction is about 36 h of heating and several days of cooling. After cooling, the silicon carbide crystals are removed, with a yield of 11.3 t per 75 t of furnace charge. The larger pieces of crystals are broken, washed, and cleaned by chemical treatment with sulfuric acid and caustic soda. The crystals are classified and screened, the finished product ranging from 6-mesh to fine powder. The outer unreacted part of the charge is combined with the next charge for the furnace.

FUSED ALUMINUM OXIDE.[5] The raw material for fused aluminum oxide abrasives such as those sold under the tradenames Alundum and Aloxite may be impure bauxite, often called *red bauxite*. The impurities, mainly iron and silicon oxides, have a great effect on the structure and properties and must be carefully controlled. Pure Bayer alumina (see Chap. 20) is also fused for particular demands, e.g., where a grinding-wheel temperature must be kept low. In any case, the aluminous material should be calcined before charging into the furnace.

The vertical arc-resistance furnace consists of a circular steel shell about 2 m high resting on a crucible carbon base about 1.5 m in diameter. The shell has a slight taper at the top for easy removal from the pig. The outside surface of the furnace is water-cooled so that the unfused alumina around the walls furnishes a refractory lining for the furnace. The round carbon electrodes are lowered into the furnace, and arcs are drawn between them and the fused furnace charge. The fusion is usually started by forming a trench in the top of the starting batch and packing it with coarse coke to carry the current. Iron borings are added to slag off siliceous impurities. The electrodes are lowered to make contact with opposite ends of the trench. As soon as the alumina begins to fuse, it carries the current, and the starting coke is rapidly consumed. A typical charge to the furnace is calcined bauxite (89%), coke (2%), and scrap iron (9%). Charge is added as fast as it fuses between the arcs, the molten

[5]ECT, 3d ed., vol. 1, 1978, p. 33.

alumina carries the current, and much of the iron and silica is reduced to form a heavy alloy and sinks to the bottom. As the level of fused alumina rises, the electrodes are raised and more charge is added, until finally the furnace is full. The current is shut off and the entire mass cooled under controlled conditions to obtain the texture desired. Although this product has the hardness 9 on the Moh scale for corundum, it is blebbular in structure and not uniform, and therefore bearings cannot be made from it. The cooled ingots are broken up by roll crushers, washed with chemical solutions, and sieved. The product is fabricated into abrasive wheels, papers, and powders or into refractory shapes by sintering.

ARTIFICIAL CORUNDUM OR SAPPHIRE.[6] For the hard bearings necessary for watches and modern instruments, *artificial corundum*, or white sapphire, is made by crystallizing pure alumina through fusion in a hydrogen-oxygen upside-down flame at 1925°C by the Verneuil process. The crystal boules are cut and polished as desired. Many gems, such as star and transparent rubies and sapphires, are also made by this process.

BORON CARBIDE.[7] This is a very hard abrasive. It first made its appearance in 1934 under the name *Norbide*. The reaction for its production is

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO$$

The boric oxide is caused to react with coke in a carbon resistance furnace at 1600°C. The product is about 99% B_4C. It finds specialized use as a powdered abrasive and in molded shapes such as nozzles for sandblasting.

BORON NITRIDE. *Borazon* is a cubic form of boron nitride formed at 6.9 GPa and 1650°C, which changes the ordinary hexagonal boron nitride to this cubic form. Its hardness is comparable with that of diamond, and it has the advantage of resisting oxidation much better. It is made by General Electric, is available in large mesh sizes, and is particularly suitable for use in production grinding.

CALCIUM CARBIDE

HISTORY. The first production of calcium carbide was an accident. In 1892, T. L. Willson was attempting to prepare metallic calcium from lime and tar in an electric furnace at Spray, N.C. The product obtained, obviously not calcium, was thrown into a nearby stream, and Willson was amazed to note that it liberated great quantities of combustible gas. The first factory for the production of calcium carbide was built at Niagara Falls in 1896.[8]

USES AND ECONOMICS. Calcium carbide is utilized for the manufacture of cyanamide by combining it with nitrogen, and for the preparation of acetylene by reacting it with water. Cyanamide is made by heating calcium carbide in an atmosphere of nitrogen (Chap. 7).

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[6]Flame Grown Gem Stones Enjoy Broadened Use in Optics and Jewelry, *Chem. Eng.* 68 (26) 26 (1961).

[7]Boron Carbide Process Temperature, *Chem. Eng. News*, 46 (6) 262 (1968).

[8]Carbide and Acetylene, *Chem. Eng.* 57 (6) 129 (1950).

Calcium carbide was used formerly in large quantities for the manufacture of acetylene, but hydrocarbon-based acetylene is now much more common. U.S. production of calcium carbide has fallen from 1×10^6 t in the 1960s to 242,000 t in 1979.

MANUFACTURE. Calcium carbide[9] is prepared from quicklime and carbon at 2000 to 2200°C.

$$CaO(c) + 3C(amorph) \rightarrow CaC_2(l) + CO(g) \qquad \Delta H = +466 \text{ kJ/mol}$$

The source of carbon is usually coke, anthracite, or petroleum coke. Coke is the most widely used. It should be compact and have a low ash content, a low ignition point, and high electrical resistivity, so that the bulk of the furnace charge will be highly resistant to the flow of energy. Thus the energy is concentrated, resulting in a more rapid and complete reaction. Phosphorus should be absent, since it forms a phosphide which is converted to poisonous phosphine (PH_3) when the carbide is made into acetylene. The quicklime is produced by burning limestone containing at least 97% calcium carbonate. Impurities such as magnesia, silica, and iron hamper production and give a less pure carbide.

The carbide furnace is not a true arc-resistance furnace, but has been developed from the familiar arc furnace. Ingot furnaces, similar to those producing fused aluminum oxide, have been replaced in the carbide industry by continuous or intermittent tapping furnaces producing molten carbide. The furnace consists of a steel shell with the side walls lined with ordinary firebrick and the bottom covered with carbon blocks or anthracite to withstand the extremely hot, alkaline conditions. Most of the larger furnaces use three-phase electric current and have three vertical electrodes suspended in the shell. Improvements include the "closed" furnace, where almost all the carbon monoxide from the reaction is collected and utilized, and Söderberg continuous self-baking electrodes, which permit larger-capacity furnaces than the old prebaked electrodes. The capacity range of the furnaces is generally between 18 to 65 MJ or higher, and a three-phase tapping furnace of 90 MJ produces about 180 t of commercial product (usually 85% carbide) per day. The approximate consumption of materials per ton of carbide is 860 kg lime, 590 kg coke, 16 kg electrode paste, and 108 MJ energy. The lime and coke are charged continuously with intermittent or continuous tapping of the liquid product directly into cast-iron chill pots of about 5-t capacity each. The carbide is cooled, crushed, and sized and then packed in 4.5- to 100-kg steel drums or up to 5-t containers for shipping.

MISCELLANEOUS ELECTROTHERMAL PRODUCTS[10]

FUSED SILICA. This very useful construction material for the chemical industries is heated to fabrication temperature in an electric furnace.

SYNTHETIC QUARTZ CRYSTALS.[11] These crystals have been grown successfully by a hydrothermal process at Bell Telephone Laboratories and Western Electric Co. by keeping a

[9]ECT, 3d ed., vol. 4, 1978, p. 505.

[10]For carbon disulfide, see Chap. 38, and CPI 2 for old electrochemical process.

[11]Higgins, 30,000 psi for Three Weeks, *Ind. Eng. Chem.* 54 (1) 16 (1962) (details given

supersaturated solution of silica in 1 *N* sodium hydroxide in contact with seed crystal quartz plates at 206 MPa for 3 weeks at a temperature of about 400°C. They are grown in special autoclaves, with a two-zone electrical heating system having a higher temperature for the dissolving zone, to bring into solution small chips of quartz, and then allowing growth on prepared quartz seed plates at about 55°C less. A satisfactory product results at a lower cost than mined quartz. Such quartz crystals are very important, indeed necessary, for use in radar, sonar, radio, and television transmitters and telephone communications. A single telephone wire can carry hundreds of messages at one time, thanks to the unscrambling powers of quartz-crystal filters.

ARTIFICIAL GRAPHITE AND ELECTRODES. Artificial graphite and electrodes are described in Chap. 5, devoted to carbon, and phosphorus is presented in Chap. 16, on Phosphorus Industries. See also Table 11.1 for a summary of the various products made by electrochemical processes.

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