Chapter 24

Surface Coatings

References:

Book (pp. 424 – 434) + Handout

Introduction

- Surface coatings include: paints, varnishes, and lacquers.
- Surface coatings are used: a) for protection from weather, and b) to increase attractiveness and aesthetic appeal of goods.
- Noah (pbuh) was told to use pitch (tar) in the ark.
- Ancient inhabitants recorded their history on walls using colored paints.
- Crude paints consisted of colored natural clays suspended in water.
- Natural resin (beeswax) was discovered. It is used in film-forming ingredients.
- Surface coatings represents a large industry with huge annual sales

Classification of Coatings

Architectural (or trade-sale) coatings

- Used to cover buildings and furniture.
- Applied to wood, gypsum wall-boards, plaster surfaces, etc.

Industrial Coatings

- Used on materials being manufactures
- Applied to metals, textiles, rubber, paper, plastics, & wood.

Historical Classification of Coatings

Paints

- Opaque solid coating applied as thin layer.
- Film forms by polymerization.

Varnishes

- Clear coatings

Enamels

- Pigmented varnishes

Lacquers

- Films form by evaporation

Printing ink

Polishes

However, the introduction of plastic resins into this industry has changed this classification

Paint Constituents

Pigment
- Gives the paint its color and opacity, and can affect the degree of gloss

Vehicle

Binder
- Holds the pigment and other additives together

Solvent
(including thinner & dispersing agent)
- Gives the paint its ability to be spread over a surface. It evaporates after application to leave behind the film of bound pigment

Additives
- Components added to impart additional resistance, drying, thickening properties.

Table 24.2 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.

Binder

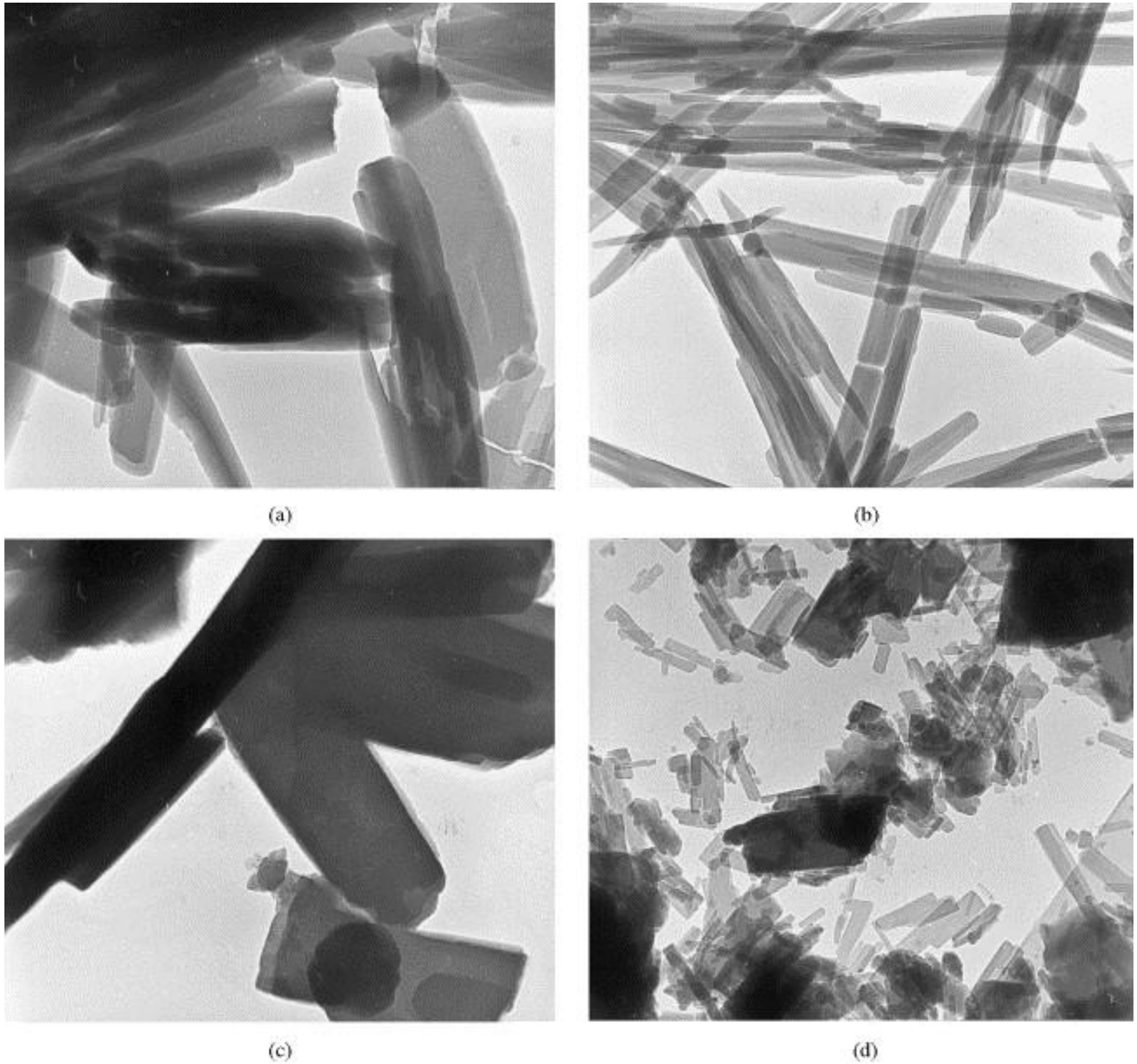
- A binder is the component in paint that forms the continuous film. It provides desired chemical and physical properties and determines the durability, adhesion, and flexibility of the paint

Acrylic	Alkyd	Cellulose	Chlorinated rubber
Emulsion	Epoxy	Natural oils	Phenolic
Polyurethane	Silicone	Styrene	Vinyl

- A paint type is usually identified by its binder, e.g., alkyd paint.

PIGMENTS

- It is a dry colorant, usually an insoluble powder
- Pigments are not only used for adding color to the coating, they are also used to improve the strength and adhesion of the paint, protect against corrosion, reduce gloss and modify application properties.
- optimum particle size of the pigment should be about 0.2 - 0.4 μm (approximately half the wavelength of light in air) to impart scattering power. (below this scattering is low).
- Pigment can have difference shapes: rod shapes (to reinforce, reduce gloss, and help sticking), plate shapes (form layers that prevent water penetration).
- There are both natural and synthetic pigments, both organic and inorganic ones.



Chisholm et al., Effects of fluorination on the properties of organic pigments
Dyes and Pigments, 1999, 42 (2), pp. 159–172

Opaque pigments

- providing color and opacity, e.g., carbon (black), TiO_2 (white)

Anti-corrosive pigments

- added to increase corrosion prevention (Zinc chromate)

Metallic pigments

- give metallic properties. Can also give anti corrosive properties by means of cathodic protection (zinc, aluminum)

Extender pigments

- to increase viscosity, reduce gloss and aid adhesion. They are also cheap (Kaolin, china clay, talc).

Lamillar pigments

- Provide a coating resistant to the passage of water and increase the tensile strength of the coating (mica, glass & iron flakes)

Property	Pigment Preference	Reasons
Brilliance and clarity	Organic	The most attractive, cleanest colors can only be obtained with organic pigments.
White & black paints	Inorganic	The purest white pigment is titanium dioxide and the most jet black, carbon. There are no organic black and whites.
Non-bleeding	Inorganic	Inorganic compounds have negligible solubilities in organic solvents. Some organics are very insoluble.
Light fastness	Inorganic	The valency bonds in inorganic compounds are generally more stable to UV light than those in organic compounds.
Heat stability	Inorganic	Very few organic compounds are stable at or above 300°C. Some decompose or melt at much lower temperatures.
Anti-corrosive action	Inorganic	All anti-corrosive pigments are inorganic.

Table 24.3 Pigments and Extenders for Surface Coatings

Ingredients		Function
Pigments White hiding pigments Titanium dioxide Zinc oxide Lithopone Zinc sulfide Antimony oxide Black pigments Carbon black Lampblack Graphite Iron black Blue pigments Ultramarine Copper phthalocyanine Iron blues Red pigments Red lead Iron oxides Cadmium reds Toners and lakes Metallics Aluminum Zinc dust Bronze powder	Yellow pigments Litharge Ocher Lead or zinc chromate Hansa yellows Ferrite yellows Cadmium lithopone Orange pigments Basic lead chromate Cadmium orange Molybdenum orange Green pigments Chromium oxide Chrome green Hydrated chromium oxide Phthalocyanine green Permansa greens (phthalocyanine blue plus zinc chromate) Brown pigments Burnt sienna Burnt umber Vandyke brown Metal protective pigments Red lead Blue lead Zinc, basic lead, and barium potassium chromates	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
Extenders or Inerts China clay Talc Asbestos (short fibers) Silica and silicates Whiting Metal stearates	Gypsum Mica Barite, barium sulfate Blanc fixe	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

Paint Constituents

Pigment

- Gives the paint its color and opacity, and can affect the degree of gloss

Vehicle (Binder, Solvent, Additives):

Binder

- Holds the pigment and other additives together

Solvent

(including thinner & dispersing agent)

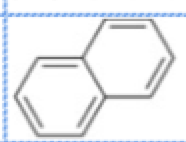
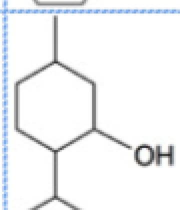
- Gives the paint its ability to be spread over a surface. It evaporates after application to leave behind the film of bound pigment

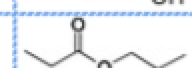
Additives

- Components added to impart additional resistance, drying, thickening properties.

Solvent

- A solvent gives the paint the ability to be spread over a large surface area.
- The solvent must be volatile to evaporate from the paint surface leaving the paint film.
- Solvents can affect the physical properties of the paint; the drying and gloss, therefore the solvent must be chosen carefully to suit the desired needs
- **Examples of solvents**:

Water	
Aliphatic hydrocarbons	
Aromatic hydrocarbons	
Terpines	

Alcohols	
Esters	
Ketones	
Ethers	
Nitroparaffins	
Chloroparaffins	

Types of Paints

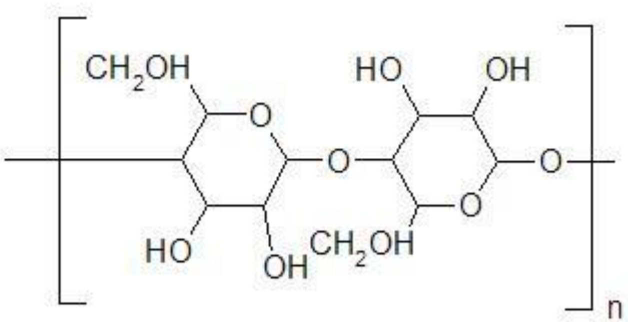
There are many different types of paint. All of which are different chemically and have different physical properties.

1) **Laquers** - General industrial finishing, cars, furniture
2) **Emulsions** - Household and industrial
3) **Oils and varnishes** - Wood and steel primers
4) **Alkyds** - Household
5) **Acrylics** - Domestic
6) **Epoxies** - Anti-corrosive
7) **Polyurathanes** - Floors, boats, corrosion resistant metal finishes, concrete and plastic coating.

1) Laquers

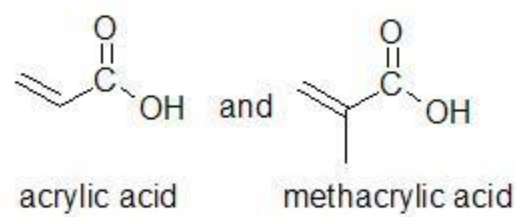
- A lacquer is a finish that can be clear or pigmented.
- It primarily consists of a hard polymer in solution.
- It dries by simple evaporation of solvents. This property makes it possible to produce a lacquer from any soluble linear polymer.

Cellulose polymers



Natural from cotton, wood, and pulp

Acrylic polymers



Synthetic

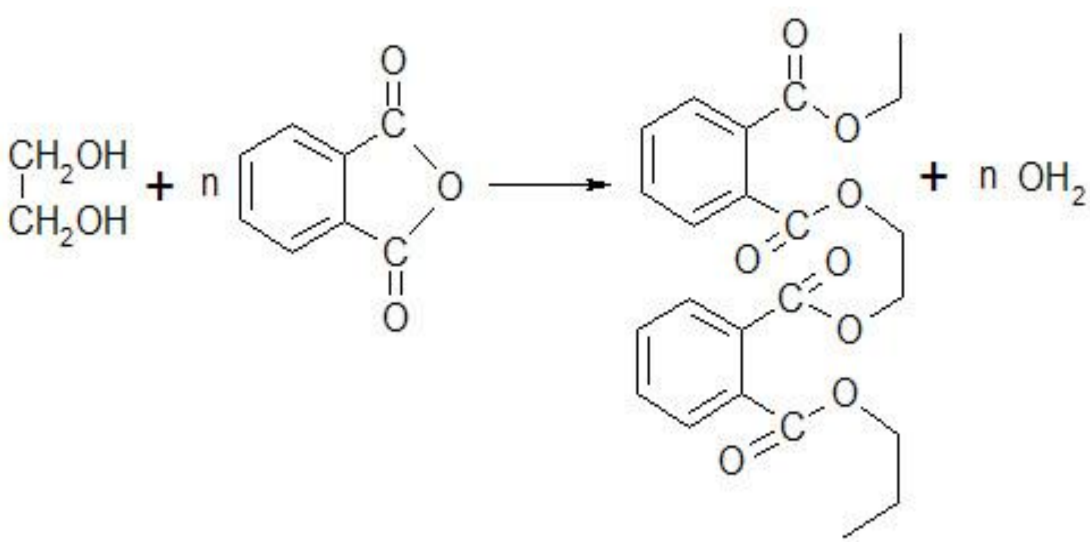
2) Emulsion paints

- An emulsion paint has two parts:
  - The dispersed phase: the droplets,
  - The continuous phase: the liquid in which the droplets are dispersed.

- The emulsion can be made in water or another non-solvent. Emulsions made in non-solvents are called non-aqueous dispersions (NADs)

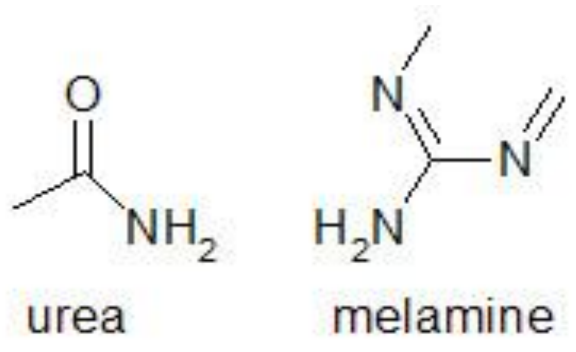
3) Alkyd Paints

- Alkyd resins are another method of improving drying and film forming potential of oils.
- Alkyd resins are copolymers of dibasic and dihydric alcohols. An oil free resin could be made from ethylene glycol and phthalic anhydride.



4) Acrylic Paints

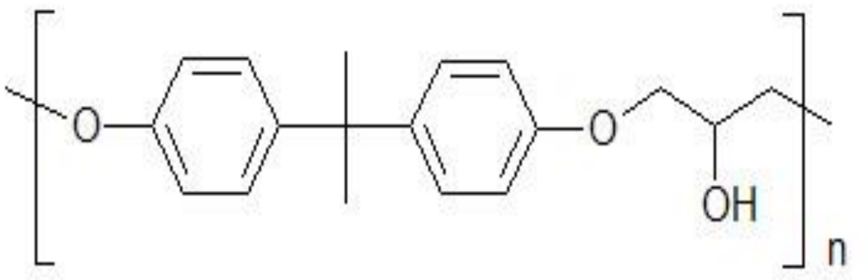
- The monomers of acrylics have NH_2 groups, e.g. urea where the oxygen is an electrophylic, and melamine where the nitrogen is electrophylic.



- The monomers polymerize through etherification and methylolation.

5) Epoxy Paints

- These can be prepared by a condensation polymerization of epichlorhydrin and a dihydroxy compound to eliminate HCl



- Short-medium epoxies can be used in stoving finishes and make excellent primers and surfaces and are used for under car finishes.
- In epoxies containing carboxyl groups, esterification takes place and cross linking throughout the polymer takes place.

6) Polyurathane Paints

- Polyester finishes contain polyester resins, which contain ester linkages. They are produced from fatty acids which are converted to diglycerides and monoglcerides when heated in the presence of polyhydric alcohols

Paint Manufacturing

- The manufacture of paint or coatings is a **physical process** that seldom involves significant chemical changes.

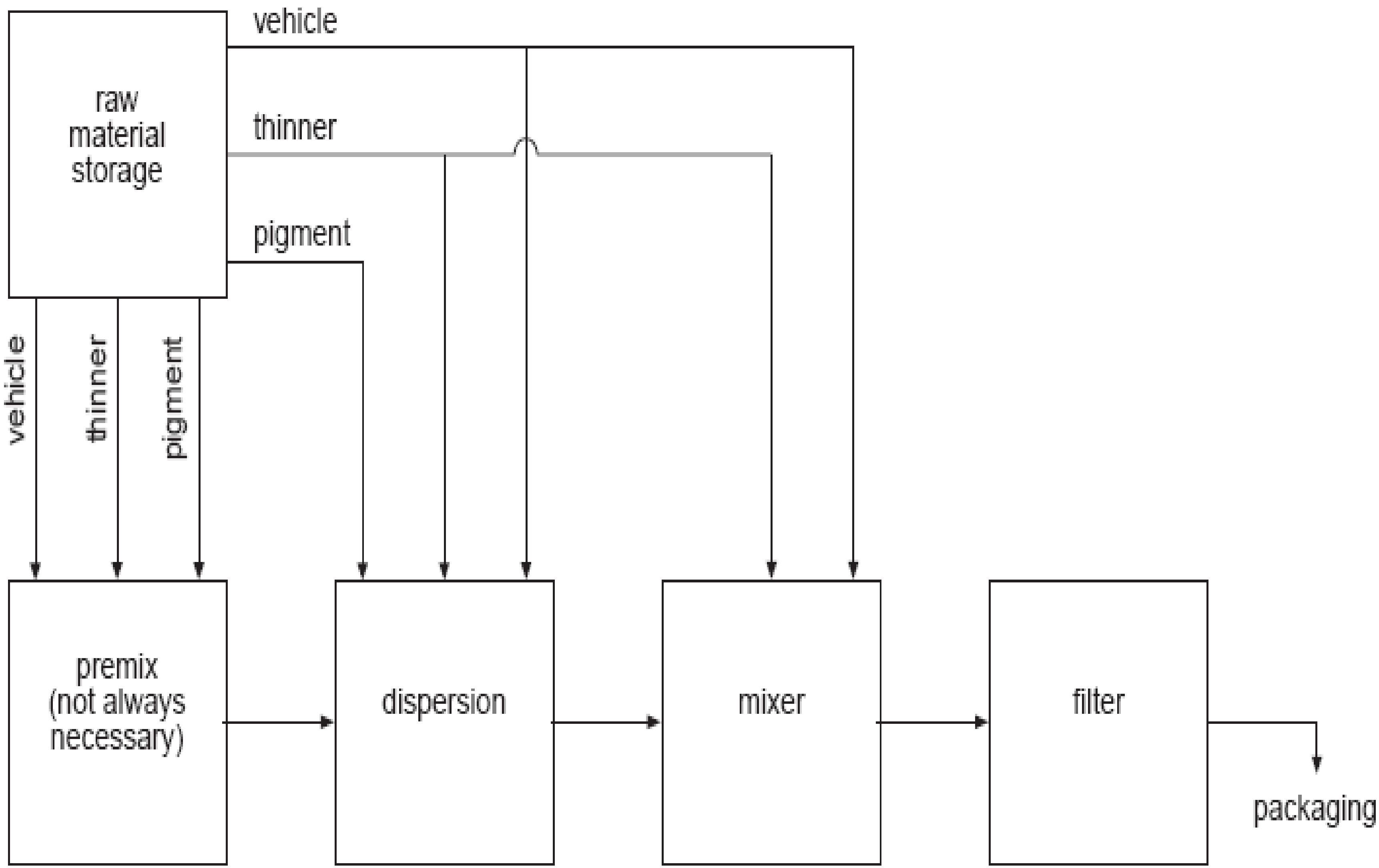
- Virtually all paint production employs the batch process, with continuous processing being quite rare.

- Manufacturing process consists of mixing, filtration and packaging steps:

Paint Manufacturing

- Clear coatings, such as varnishes, are made by mixing specific ratios of resin binders with volatile solvents, using a mechanical agitator in a mixing tank. Once mixed, the batch is pumped through a filter and packaged for sale.

- For opaque (white or colored) paint is manufactured, the process is the same as for making varnish except that pigments are first dispersed in a portion of the vehicle. The batch is finished by mixing the balance of the vehicle into the pre-dispersed pigment/vehicle mixture.



raw material storage
vehicle
thinner
pigment
vehicle
thinner
pigment
premix (not always necessary)
dispersion
mixer
filter
packaging

Pigment Dispersion step

- **Why pigment dispersion is critical?**
- Each dry pigment particle is actually a cluster of many smaller particles; the objective is to separate them from one another so that the surface of each small particle can be wetted with the vehicle and the particles can be evenly distributed throughout the paint.
- This is accomplished by applying powerful mechanical forces using dispersion machinery of several different designs, e.g. High-speed disperser (a shaft with a disc-like toothed blade on one end.)

Pigment Dispersion step

- **Why pigment dispersion is critical?**

- When the blade is spun at high speeds in the viscous pigment/vehicle mix, shearing forces are produced at the surfaces of the blade.
- Often it is necessary to make a premixed paste of pigment/vehicle using a high-speed disperser. This paste is then fed into one of the other types of dispersion machinery.

Dispersion Stabilization

- Once dispersed, pigment particles have a tendency to associate, or flocculate, into loose clusters or to settle into a hard cake.
- Dispersion stabilization
  - Special additives are often necessary to enhance dispersion stability.
  - In water-thinned paint, stabilization is accomplished by imparting like electrostatic charges to pigment particles so that they repel each other.
  - In solvent-thinned paint, stabilization usually depends on steric hindrance, with molecules of binder adsorbing onto the pigment particle surfaces to form immobile envelopes around the particles. These envelopes of binder act as a physical barrier to particle association.

Filtering & Packaging

- The filtering step provides a way to remove any undispersed particles or extraneous in the batch.
- Filtration methods:
  - One often-used method employs vibrating screens with 40–300 mesh per square inch as strainers to separate the unwanted materials from the paint.
  - Another filtering method allows the paint to drain through felt bags.
  - Sometimes the paint is passed through cylindrical cartridges of porous material; where the paint filters through the walls of the cartridge, leaving the separated material in the container.
- Once filtered, the paint batch is packaged.

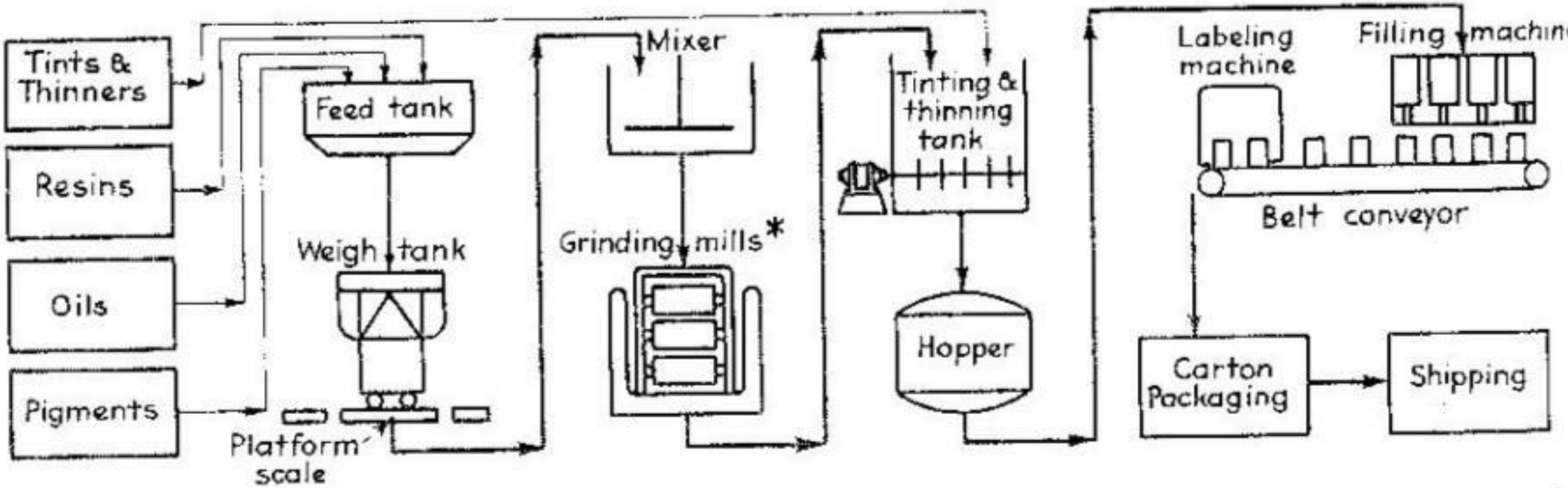


Fig. 24.1. Flowchart for the mixing of paint. NOTE: Because a complete paint factory consumes upward of 2000 different raw materials and produces ten times as many finished products, it is not possible to give yields, etc.

**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.*

Paint Drying

- The reason a paint goes dry is either due to the evaporation of the solvent or a chemical reaction to the binding medium, or a combination of both.
- The coating can be *air dried* or *force dried* at temperatures of up to 65°C. At temperatures above 65°C the drying process is called *stoving*.
- A paint can dry in one or a mixture of the following four methods:
  1. Solvent evaporation
  2. Oxidative drying
  3. Chemical curing
  4. Coalescence

1) Solvent evaporation

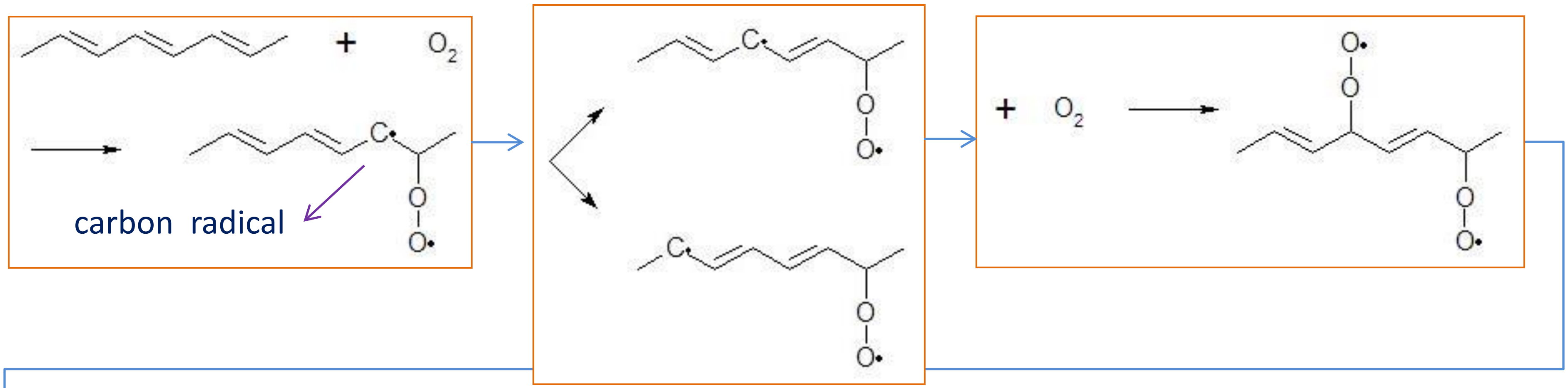
- Some paints can dry solely by the evaporation of the solvent to leave a film of non volatile solids; but a chemical change does not take place.
- These paints are referred to as ***reversible*** or ***nonconvertible*** paints.
- This is because if the solvent is reapplied then the coating will re-soften.
- These types of paints possess linear or branched polymers such as chlorinated rubber and vinyl paints.

2) Oxidative drying

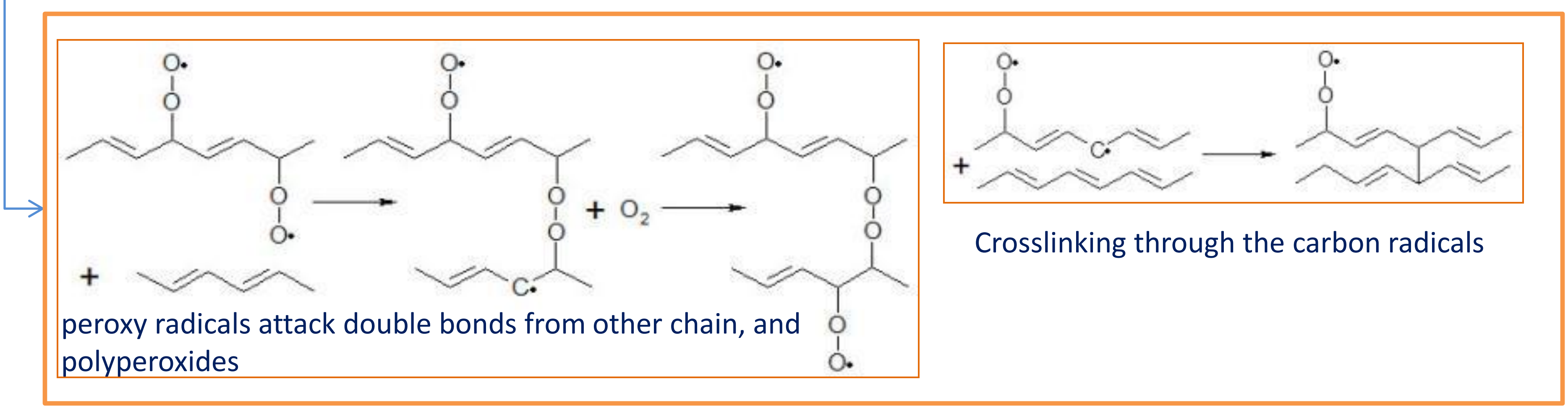
- This drying method often occurs after solvent evaporation.
- Oxygen from the air causes a polymerization reaction within the binder. This occurs with the aid of driers in the paint and forms a hard film.
- These types of paint are called ***nonreversible*** or ***convertible*** paints, as they do not re-soften if the solvent is reapplied.
- This is due to the chemical change which occurred as the polymerization took place.
- Paints that dry in this process contain complex polymers.
- Drying mechanism based on cross-linking of chains

Cross-linking

Initiation **Propagation** **Oxidation to Peroxy radical**



Cross-linking polymerization reaction



Termination: Cross-linking ends when two radicals react with one another

3) Chemical curing

- This process is similar to the oxidation process, except a different chemical is used to polymerize the paint rather than oxygen.
- This chemical can either be:
  - an additive of the paint, which is activated via an external source of energy e.g. heat, uv light,
  - or the chemical can be applied prior to application, these are called two-pack systems.
- The paint additives that provoke chemical reaction are called activators. They are usually chemicals which decompose and form free radicals, which in turn initiate an addition polymerization reaction.

3) Chemical curing – continued

- Catalytic chemicals (called driers and accelerators) are other chemicals which determine the speed of which this polymerization reaction takes place.
- Driers and accelerators are added to speed up the drying reaction. Catalysts alter the speed of a reaction without being used up themselves.
- Inhibitors are added to slow the reaction down. They react with the free radicals that are formed thus preventing them from initiating addition polymerization reactions. Inhibitors undergo chemical change in the process.
- Anti-skinning agents are mild inhibitors used in oxidative drying to increase stability whilst in the paint can.

4) Coalescence

- This process occurs after initial solvent evaporation.
- It is addition of a high boiling solvent that gives the monomers more fluidity and can move closer together to react.
- The newly formed polymers go on to react with themselves and form a continuous cross-polymerization network.
- Examples of these types of paints are acrylic and vinyl emulsions.