19 Detergent Processing

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19.1 INTRODUCTION

The manufacture of laundry detergents has changed significantly over the past 20 years, but the appearance of the products has not although a number of different product forms have been introduced. Even with the growth of the liquid form, the main form is still that of a powder and remains the largest growth area globally, especially in the developing regions.

Powders have a number of advantages in that they contain a relatively large proportion of inorganic materials, such as builders (water hardness removers), alkalinity sources (e.g., sodium carbonate), and bleaches (sodium percarbonate), which tend to be cheaper than petro- and oleo-derived materials. In addition, due to their low moisture content, it is much easier to include a range of more complex or metastable ingredients such as bleach and enzymes and keep them stable during the trade. This is important since the products must remain stable for about 12 months and beyond after making. Products can experience wide ranges of temperature during transportation, particularly when exposed to sunshine, as well as in warehouses and retail outlets. Temperatures can vary from −10 to +50°C. However, this then requires careful control of moisture ingress since the products are normally made with very low relative humidity and they tend to attract water vapor from outside the package.

Another advantage of the powder form is the formulation consistency. When segregation is well managed there is little danger of separation of ingredients, whereas liquids are more prone to phase separation, and although a lot of progress has been made in this area, phase separation is still poorly understood.

There is also, especially in the developing countries, a large market for syndet bars. These are similar to soap bars, but are much bigger with the necessary ingredients for cleaning clothes. They are mainly used in hand washing, where they can be easily applied in a concentrated form, and also for rubbing soiled garments to assist in cleaning.

Recently, a number of more convenient forms have been introduced with varying success, mainly driven by local consumer preferences. These include highly compacted powders (such as Kao's Attack in Japan), uniform pelletized products (such as Henkel's MegaPerls in Germany), and unit dose tablets and liquid pouches (such as Procter & Gamble's (P&G) Ariel Liquitabs in the United Kingdom). Each of these forms presents unique challenges during their manufacturing. Although in each case, the same principles drive the process innovation and manufacturing operation. These include

Capital minimization. Since this consumer area is of considerable size, the manufacturing plants tend to have large throughputs, necessitating substantial capital investment. This not only impacts on product cost but also has business risk for new ventures and the time to market in a fast moving, highly competitive market. Thus, there is a drive for high production rates and low capital investment, typically pushing the boundaries of experience in areas such as spray drying, agglomeration, tabletting, and packaging.

In addition to the need for high production rates, there is also the need for high capacity utilization and process reliability. Given the high number of unit operations in a detergent plant, each of which can stop the process, it is important to understand and eliminate causes of downtime. Today, the best plants operate with a capital utilization of over 95%.

Formulation flexibility and agility. Typically, one plant will make a range of different products, either under different brand names or under a range of custom-made "own-label" products. This is made more complicated in that, typically a lot of the ingredients are sourced from a number of different suppliers and some of these raw materials can vary in terms of activity and quality. Thus, a process must be flexible enough to cope with such variations, while still producing the consistent quality a consumer demands. In addition, the competitiveness of the market place means that competitors are continually developing new formulations and new ingredients to gain an edge in the market place. This again results in challenges regarding the equipment design and plant layout to allow fast and low cost changes to new formulations.

A recent trend has been in the area of customization, whereby the consumers prefer to have a number of different variants to meet their desire for variations such as different perfume types. Achieving this without a large expansion of capital investment is a significant challenge to large-scale producers.

Finally, inventory costs are such that plants no longer have the luxury of producing one formulation for a number of days before switching to another. Typically, plants are required to make a number of different products within one shift, which puts pressure on being able to rapidly change from one product to the other without losing out on quality.

Packaging. With few exceptions, the product is packed on-site into cartons, bottles, or sachets as appropriate. Since numerous sizes are sold on the market, a number of packaging lines are needed. Typically, a packaging line will not run at the same speed as the production line, and therefore, a buffer is needed between the two operations. Even if this were not the case, hard linking of the two is not recommended as packing lines tend to have much more breakdowns than the production line. Coping with this buffer stock and feeding the material to the right packing lines is a considerable logistics and control challenge.

Initiative management. Another area is that of managing change from one product range to a new one to stay ahead of competition. A modern, large production facility is very complex and bringing in new ingredients can not only add to the capital cost but also impact on the logistical operation of the plant. Mathematical models are now used to predict any bottlenecks and resolve them ahead of any building work as well as minimize the impact of construction work on the day-to-day operations of a plant.

Another balance has to be made between buying a turnkey unit from one of the manufacturers and custom design. Typically, the larger producers have such an extensive experience of operating their plants plus a knowledge of the new ingredients that custom design is the preferred option. It also aids in the maintenance of trade secret information.

Quality control. Consumers expect consistent quality, and it is much harder to gain new consumers than maintain existing ones. Thus, maintaining quality is very important. Although the pressure to reduce inventories means that it is costly to hold the finished product while it is being checked for quality before releasing to be shipped. Consequently, a lot of research has been done, and is still being developed, on rapid product characterization tools to minimize the hold up time of a product once it is made. In addition, online monitoring and feed-forward control systems greatly minimize the chances of producing off-specification material. A similar attention to raw material quality is just as important in this area.

Operating costs. Highly automated systems can run with low manning requirements but typically need highly qualified people to maintain and monitor the processes, and require a high capital investment. Highly manual systems are much more flexible and require lower investment, but higher levels of manning. Getting the balance right to minimize cost, while maintaining flexibility and quality is very complex even for a simple recipe, and therefore, each situation needs to be analyzed individually, taking into account the varying local factors including import duties, scale of operation, and labor costs.

Energy costs have always been a factor, and the growing cost of energy is having a big impact on the process design and plant operation in the continued drive toward reducing added cost and providing the consumer with a better value.

Safety. Finally, all these must be achieved without compromising on safety, for the worker, equipment, and environment. Hygiene is particularly important for the health of the worker, especially to protect against fine, alkaline dusts, and enzyme particles in the atmosphere, whether from particulate dust or aerosols in liquid-making products. Spray drying combustible material has led to fires in the spray drying towers, resulting in costly repairs and downtimes. Environmental emissions can be kept to a minimum by good process operations and material capture and internal recycle.

The introduction of liquids has resulted in a new concern—that of bacterial contamination. Although detergents are designed to be nondigestible and therefore consumer safety is not a problem, contamination can lead to off odors and off-putting appearance of liquid products leading to consumer dissatisfaction, and this has to be avoided.

19.1.1 Surfactant

Although each product form encompasses a number of different raw materials, the one material that is common to all forms is linear alkyl benzene sulfonate (LAS). This has been the main workhorse for over 50 years, providing the basic surfactancy demanded for cleaning. It has the advantages of being available in large volumes, is relatively cheap, has a good safety and biodegradability profile, and is solid at room temperature. It is also, typically the only raw material that is chemically altered before adding to the rest of the ingredients, and is summarized in the following text. The rest of the ingredients are aqueous solutions such as sodium silicate, powders such as zeolite of ~5–100 μm, or special particles such as bleach materials with a particle size of ~500 μm to match that of the blown powder.

Typically, plants would buy in the alkyl benzene and sulfonate on-site using either oleum or liquid SO_3 before neutralizing with caustic solution. The reactions are highly exothermic and can cause the coloration of the product if temperatures are not controlled. Thus, a dominate bath approach was used to control the quality since consumers do not associate a brown-coloured product with good cleaning power!

Concerns regarding the safety of transporting aggressive chemicals such as oleum, as well as maintaining a good process control has led to a number of different process options being used.

First, the large producers have tended toward producing SO_3 on-site by burning sulfur and using falling film reactors for sulfonation. This is a high capital investment and a complex process to run and maintain, but in terms of product cost it more than pays back.

For smaller producers, a different approach is taken. Fortunately, the acid form of LAS is quite stable and has a low viscosity at an active level of ~98%, and is less aggressive compared to oleum. This material is shipped in drums or bulk to detergent plants for use in product making.

It has one other advantage in that it can be neutralized with sodium carbonate without overheating as the reaction rate is relatively slow. This "dry neutralization" reaction is used to good effect in making high-density surfactant agglomerates for high-density products with relatively low capital since the surfactant contains very low amounts of water, and therefore, there is no need to include drying equipment to remove water from the system.

19.1.2 Product Forms

The main product forms, with their pros and cons and the specific challenges in manufacturing are covered separately in the following sections.

19.1.2.1 Powders

As mentioned previously, powders are the largest volume produced globally and are still seen as the form with the largest growth potential. The main process is to form a concentrated, aqueous slurry of most of the raw materials and spray dry it in a countercurrent tower. This has the advantage of producing a relatively free-flowing powder with most of the ingredients contained inside, and therefore is less prone to the effects of segregation. The high surface area provides rapid dissolution rates and the process is highly flexible with respect to formulation. Typical bulk density of the product is ~500 g/L with median particle size of ~400 μm. Both these can be varied slightly by changing process conditions.

Certain ingredients such as perfumes, enzymes, and bleach cannot be processed in this way, and therefore, they are added to the spray dried product (blown powder) afterward.

Typically, the products are white but some producers add dyes to form colored blown powders. This has the disadvantage of requiring cleanouts between products if the same unit has to produce a white product as well.

These units typically require high capital investment, and therefore need a large market to provide satisfactory economics.

Products are sold in a variety of packaging forms, from single-use sachets to >10 kg cartons. Sachets have an advantage of providing a good moisture barrier protection when compared to cartons, although a lot of cartons are made with an internal polymer layer to provide some resistance to moisture ingress.

19.1.2.2 Compact Powders

The move to lower volume products really started in Japan (Figure 19.1), where more compact boxes were more desirable by consumers due to the lower storage space requirement.

This then moved to numerous other developed markets. The desired bulk density was beyond that achievable by normal spray drying, and thus various process innovations were developed. These included taking the blown powder and compacting it, using roller compactors, followed by grinding and sieving to achieve the right density. Although being relatively simple, the process was not very efficient due to the recycle level, and thus, other processes such as agglomeration were developed. The extension of this concept was reached in Germany where Henkel (Figure 19.2) produced a novel-looking product by extruding the ingredient mix into noodles, which were then broken up and rounded.

FIGURE 19.1 Kao's Attack® product.

FIGURE 19.2 Henkel's Megaperls®.

This latter process is simple in concept but technically challenging since extrusion demands certain rheological properties and the low surface area/volume is not conducive to fast dissolution. Thus, numerous process and formulation innovations have been required to achieve the desired product quality, the magnitude of the challenge being evident from the large number of patents in this area.

19.1.2.3 Tablets

The laundry tablet form is the ultimate in compaction. This also makes dosing simpler for the consumer and is less messy. However, there is a balance to be made in that high degrees of compaction are typically needed to ensure a tablet that is strong enough to resist fracture on handling, yet, this level of compaction restricts the rate at which a tablet can dissolve fast enough in the relatively low-shear environment of the washing process. Typically, compaction is kept to the minimum required to form a strong enough tablet, and various coatings and ingredients are added, respectively to improve the fracture resistance during transportation and to enhance dissolution by causing the tablet to swell and crack once it hits the water.

Controlling the physical properties of the product to be compactable at low pressure, as well as being able to do this at high enough production rates to be financially viable places a number of tough technical challenges on the process engineer and the manufacturing plant.

Despite the growing acceptance of this form in the automatic dishwashing market, it is of limited acceptance in the laundry market.

19.1.2.4 Liquid Detergents

Although being widely used for light-duty cleaning for a long time, the so-called heavy-duty liquids (HDL, Figure 19.3) have only been of significant impact for ~20 years.

This was not helped by the early design of horizontal drum washing machines, where the product leaked out of the dispenser drawer and into the machine sump, thereby significantly reducing the amount of material in the wash drum for cleaning. Various producers resolved this with machine dosing devices until the machine manufactures caught up, and it is a good example of the interrelationship between the producers and the machine manufacturers.

Liquids have numerous advantages over powders: they are quick to dissolve and do not have a tendency to cause product gels in dispenser draws or machines—a major consumer concern. The lack of inorganic components reduces the residues on fabrics for an improved fabric feel, and this product form has grown especially in North America.

The big challenge is the ingredient compatibility, especially between enzymes and bleach stability in an aqueous matrix, as well as phase stability. In the latter case, it is possible for various

FIGURE 19.3 P&G's Tide® liquid detergent.

FIGURE 19.4 P&G's Ariel® liquitabs.

ingredients to separate out on aging and thus provide poor performance for the consumer. These product forms are much less flexible compared to powders and therefore demand a much greater degree of interaction between the product designers and the process engineers for success.

They are manufactured either in batches or continuously and there are strong proponents for both processes. However, one advantage is that capital investment for small-scale operations can be much lower than for the spray dried granules, and thus, small producers can enter the market more easily with this form.

19.1.2.5 Liquid Pouches

The initial popularity of tablets led to the logical question as to whether liquid detergents could be made available in a unit dose form. The resolution came with the development of a polymer pouch using polyvinyl alcohol (PVOH) as the container (Figure 19.4).

PVOH has some unique properties in that it is very water soluble, but it can cope with small amounts of water in the entrapped liquid; it is highly elastic, and therefore can be stretched, filled, and then be made to spring back to form a taut pillow shape; and its chemistry can be modified substantially to make it compatible with the detergent product. Nevertheless, achieving high production rates with low leakage levels has been a considerable challenge. Typical problems include quality control of the incoming film to avoid pinholes and defects for preventing leakage on stretching and being able to seal the pouches at high production speeds that are required to keep the capital investment low. Recycling off-standard products and returns from the trade is also more challenging and makes the whole operation more complex. Despite the difficulties, there are a large number of consumers who prefer this simple, no mess means of dosing product to the washing machine.

19.1.2.6 Syndet Bars

These bars started out basically as a block of solidified soap in a convenient to make and handle form, often shaved for placing into washing machines to aid dissolution. However, with the development of synthetic surfactants and detergency aids such as polyphosphates, the developed markets moved toward synthetic detergents, which are sold either in large bar form, of ~500 g, or can also be cut into sections for customers with limited cash (Figures 19.5 and 19.6). Here, the solid bar is anything but rapidly soluble, which is benefitial for hand wash and long usage life as the bar is used to scrub clothes as well as generate high concentrations for difficult soil removal.

A laundry detergent bar, used directly on stains for hand washing of fabrics, is one of the oldest versions of laundry detergent and is still very prevalent in developing countries. The earliest versions of laundry bars were made of soap. Since the late 1960s, synthetic detergent bars started replacing the traditional soap bars. In Philippines, India, and other Far East countries, synthetic detergent bars are the dominant form. In Latin America, Africa, and China, soap bars are still the major form of bars used. Recently, a trend toward soap-syndet combo bars is gaining ground in some markets. However, conversion to granules and powders is taking place at a steady pace in all the regions of the world.

FIGURE 19.5 P&G's Mr. Clean® syndet bars.

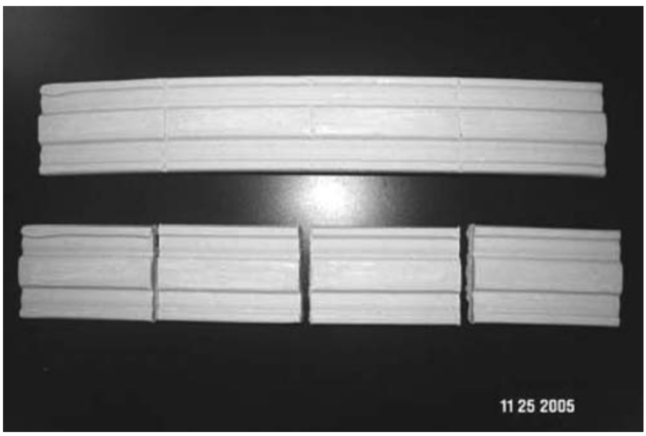


FIGURE 19.6 Typical unwrapped syndet bars.

The basic bar-making process involves neutralization of LAS sulfonic acid (in the case of LAS, containing bars) using sodium carbonate, and mixing it with all other ingredients in a particular sequence followed by extrusion of the mixed mass through an extrusion die. The bars coming out of the extruders are cut to the desired size and stamped with the logo and cooled in trays or on a belt in a cooling tunnel before packing. During processing, the actives are exposed to relatively high moisture, high temperatures, and high-shear stress. An alternative process is to compression mould the mixed mass. This process is more compatible with many actives such as bleach and enzyme due to the relatively low-temperature processing. These processing conditions, and the need to maintain chemical and physical stability of the bar through repeated wetting/drying cycles (as the bar is used over multiple days) represent key challenges to the formulator.

Synthetic detergent bars deliver much of the same chemistry to the wash as heavy-duty granules. The primary cleaning power comes from anionic surfactants along with phosphate builders such as sodium tripolyphosphate (STPP) and tetra sodium pyro phosphate (TSPP). In India, Latin America, and Africa, LAS is used as the main surfactant, whereas in the Philippines, a combination of alcohol sulfates (preferably coconut based) and LAS is used as the surfactant system. In premium bars, STPP is the preferred builder as it offers, in addition to excellent hardness binding capacity, very good processability and control of in-use physical properties such as bar wear rate and sogginess or mushiness. In low-priced bars, a small amount of STPP is sometimes used for processability reasons. Performance-enhancing actives, such as chelants, polymers, fluorescent whritening agent (FWA), and recently, enzymes and bleach are often included as well, as are sodium carbonate, sodium sulfate, inorganic fillers such as calcite, talc, and clay. Carbonate and sometimes sodium silicate provide the necessary alkalinity, whereas the inorganic fillers give "body" to the bar and also act as process aids.

Surfactant level varies from 10–15% in low-priced bars to 20–30% in premium bars. Where a combination of surfactants is used, as in the Philippines, typically a mixture of alcohol sulfate and LAS is used in a ratio of 50 : 50–85 : 15. Bars containing only AS as the surfactant are very brittle and need a high amount of humectants such as glycerine or addition of hydrotropes to reduce the brittleness. STPP/TSPP level ranges from 0–3% in low-priced bars to 15–30% in premium bars. The moisture level in the bars varies from 3 to 12%, carbonates typically from 10 to 25%, and fillers such as calcite, talc, and clay fill the rest of the formulation. Because the presence of free water in the bars can lead to mushiness during production or use, a variety of desiccants and adsorbent materials have also been added to bars to control the moisture. Examples include phosphorous pentoxide, sulfuric acid, boric acid, and calcium oxide as well as a variety of clays.

19.1.2.7 Other Product Forms

Various novel forms such as gels, foams, and sheets have been tried in the past, each presenting unique challenges. However, none of these has resonated with consumers to date, and therefore, these remain niche products of low volume and will not be considered further in this chapter.

19.2 DETERGENT POWDER PROCESSING

Detergent powder processing, as mentioned earlier, is composed of a number of basic operations such as spray drying, agglomeration, and finished product making and handling. Each operation is considered in the following in text.

19.2.1 Processes for Making Detergents

19.2.1.1 Spray Drying

19.2.1.1.1 Introduction

Spray drying is the most important process used in the manufacture of detergent granules. It is the process route by which the main component of the vast majority of granular products is produced and the spray dried powder properties dominate the physical characteristics of the product. In the developed world, it survived the rise of the compact, agglomerate-based products, in the 1990s, the consumer preferring the lower-density product offered by spray drying. In the developing world, granular, spray dried products are the detergents of choice, and increasing prosperity in these regions has driven increased production volumes. Spray drying processes are capital intensive and typically quite large as shown in Figure 19.7.

The detergent spray drying process itself is well established. It was introduced about 60 years ago. Over the years, the process has been optimized considerably. In particular, major improvements have been made to production reliability, whereby plant utilization has increased from ~45 to over 90% in some locations due to the application of reliability engineering tools to minimize downtimes in production. The production rate of individual units has also increased quite dramatically as limits are understood and overcome by interventions such as airflow modifications and multilevel spraying. Rates of over 80 t/h are now achieved in single spray drying towers today, although smaller tower rates can be as low as 1 t/h. These two factors, along with radically improved transportation networks, have led to some significant consolidation of production units in the developed regions of the globe.

FIGURE 19.7 A typical manufacturing unit for spray dried detergent powders.

Despite its maturity, the spray drying process still has many challenges ahead. Formulations continue to change at an ever-increasing pace and frequently push the boundaries of the known operating envelope. Additionally, as the market becomes more segmented, the number of formulas increase. This, together with the drive to just-in-time production schedules (to minimize inventory) drives down production run length. Thus, start-up and shutdown times on these large-scale production units need to be significantly reduced to maintain plant utilization as well as good product quality.

19.2.1.1.2 Blown Powder Formulation

The spray dried granules are often known as blown powder. The components of blown powder are those of the detergent formulation that are robust to the operating temperatures within the tower. The core components are as follows:

Anionic surfactant—most often LAS
Builder—zeolite or STPP
Inorganic salts—sodium sulfate, sodium carbonate, sodium silicate
Polymers—polyacrylate, carboxy methyl cellulose

The properties of the slurry and the subsequent blown powder are dominated by the interaction of the LAS, which forms a liquid crystalline phase with the other ingredients within the slurry. Consequently, small quantities of some minor ingredients such as polymers, hydrotropes, and cosurfactants can have a significant effect on the slurry properties such as its rheology, and therefore, the amount of water required in the crutcher mix.

The structure of the blown powder is also dictated by the crystallization of the inorganic phases. In this respect, silicate and polyacrylate both improve granule crispiness and toughness.

19.2.1.1.3 Process Description

The spray drying process enables efficient, countercurrent, contact of an atomized detergent slurry with hot air, producing a detergent granule. The process itself can be split into five sequential operations as follows (Figure 19.8):

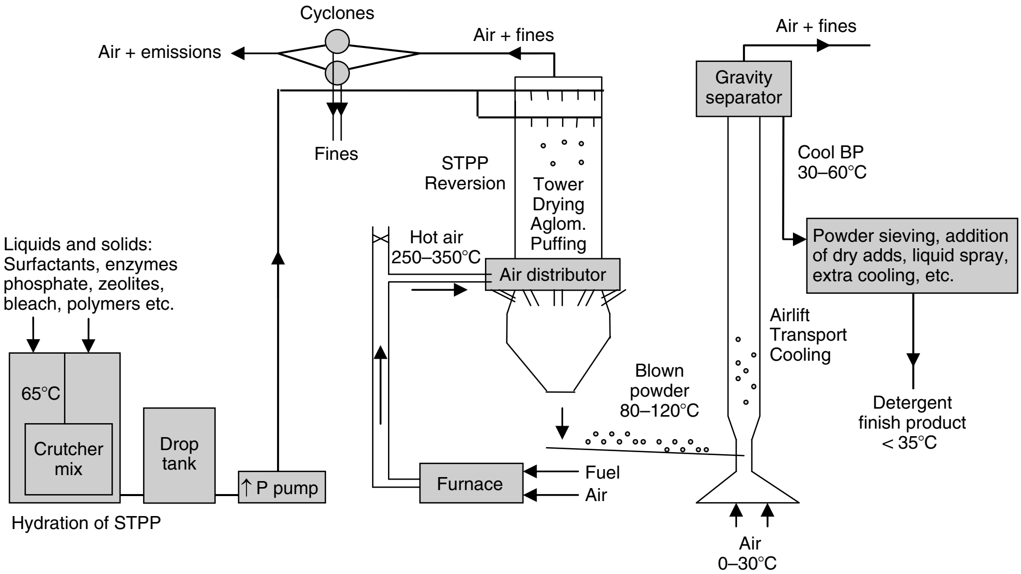


FIGURE 19.8 Schematic drawing of a spray dried detergent unit.

Slurry making
Pumping
Atomization
Drying
Cooling and classification

These operations are considered in the following text. Raw material storage, handling and dosing are common to many industries are not considered in this chapter.

19.2.1.1.3.1 Slurry Making

The objective of this process is to make a homogeneous slurry of consistent composition and aeration, with minimum water content, that is, the lowest possible drying load. The first challenge of incorporating powder and liquid raw materials is achieved by a continuous or batch mixer, known in the industry as a crutcher. Both of these types of mixer have been optimized by experience, and advocates for both methods will argue their benefits, for example, in minimizing aeration or in their ability to handle lower water content slurries. In reality, there are rarely two mixers that are the same and it is unclear whether either has a fundamental advantage. Over recent years, as production scales have increased and control technology improved, the systems for dosing these mixers have become highly automated and more accurate. In addition, the increase in production rates in the drying tower has meant considerable work to reduce the dosing and mixing times, and therefore avoid large capital investment and plant shutdowns during upgradation. From the crutcher, the slurry is transferred to a holding tank, sometimes known as a drop tank; here, further mixing occurs and the slurry ages allowing various phase formations and crystallization processes to take place. Filtration is carried out to achieve further homogenization and ensure that the spray nozzles do not block the final stage of slurry making. Typically, magnetic filters are used followed by disintegrators, which incorporate a filter with a smaller orifice size than the nozzles. Systems for adjusting slurry temperature and aeration, by injecting stream or air into the slurry, can be incorporated at any point in the process.

19.2.1.1.3.2 Sodium Tripolyphosphate Products

STTP was, for a long time a significant part of detergent formulations. Not only is it good at controlling water hardness, it also has good sequestering properties and provides buffering capacity and a crisp, robust granule. It is still used in many countries and can present processing challenges.

The reason for this is that it hydrates to the hexahydrate during the slurry making and continues to hydrate after the making process. Such hydration reduces the free water in the mix and thus can have a big impact on viscosity. The material has two different crystalline phases—I and II. The former hydrates at a much faster rate than the second. The hydration rates in both cases are sensitive to temperature also—lower temperatures giving more hydration.

Too much hydration in the slurry can lead to extremely high viscosities, even beyond the processing capability (instances are known whereby the slurry has set solid due to overhydration). In addition, the dehydration of the hydrate during spray drying can lead to degradation of the STPP to poorer performing molecules. This is known as reversion.

In contrast, too little hydration can lead to the production of a poorly hydrated blown powder. This then tends to pick up moisture and hydrate on storage and can lead to overheating and caking. Therefore, good control of STPP hydration is crucial for steady operation and for producing a good-quality product. Thus, it is important to have a consistent quality of the raw material.

19.2.1.1.3.3 Pumping

As a result of the low moisture content of the slurry and the short mixing times, the slurry can have inorganic lumps, which would block the atomization nozzles. The typical way of resolving this is to pump the mix through a filter and provide a disintegrator to break up any such lumps before passing to the main slurry pump. To achieve the high pressures (up to 100 bar) required for atomization, one or more piston pumps are typically used. In most cases these require a booster pump, typically a positive displacement pump, to keep them efficiently filled with viscous aerated slurry.

19.2.1.1.3.4 Atomization

The objective of the atomization process is to create drops small enough to dry in the spray drying tower. This is done with a number of high-pressure nozzles known as hollow-cone pressure swirl nozzles. These nozzles are distributed at one or more levels within the spray drying tower and have to be sufficiently distant from the wall to avoid buildup caused by wet drops sticking before they have dried sufficiently. For this reason, and for reasons of residence time, smaller towers typically run with smaller nozzles.

Two problems are often encountered with spray nozzles: nozzle wear and nozzle blockages.

Nozzle wear. The abrasive slurry causes the nozzle tips to become enlarged and rounded with time, even with the hard tungsten carbide or yttrium carbide nozzles that are typically used. This wear causes bigger drops, wall buildup, and poor product properties. This is particularly the case with zeolite-based slurries where nozzles must be carefully monitored and changed every few weeks.

Nozzle blockages. Occasionally nozzles get blocked, therefore several spare nozzles are usually kept available during operation. With a suitable filter size, good operating, and clean-out practices, these occurrences can be minimized. However, most towers have inspection windows that allow operators to monitor atomization during operation. Alternatively, constant monitoring of the spray dried particle size can indicate upstream problems before their impact can get out of control.

Typically, a nozzle will produce a wide range of fine droplets, which do not have time for the surface tension to pull them into a sphere before they are dried. In addition, the different sizes tend to agglomerate in the turbulence, and thus, a spray dried granule is more like an irregular-shaped bunch of grapes. Problems can occur if the nozzles are too close to one another in the tower, leading to overagglomeration and hence too many coarse particles. Figure 19.9 shows a typical sample of granules.

On further magnification, the knobbly shape and internal porous structure can be seen as in Figure 19.10—a scanning electron microscope (SEM) picture.

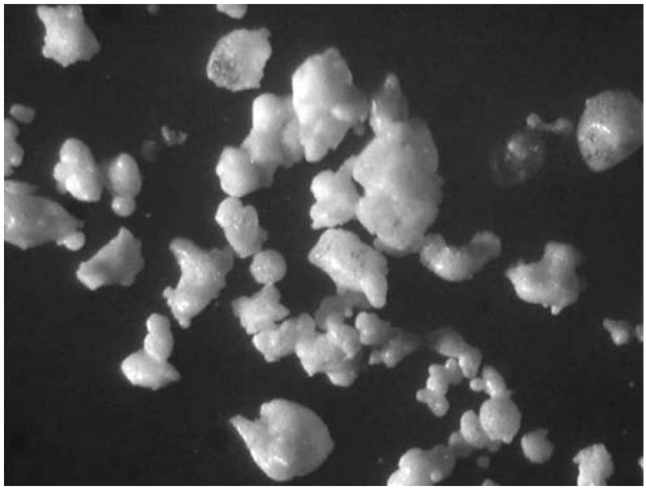


FIGURE 19.9 Typical spray dried detergent particles.

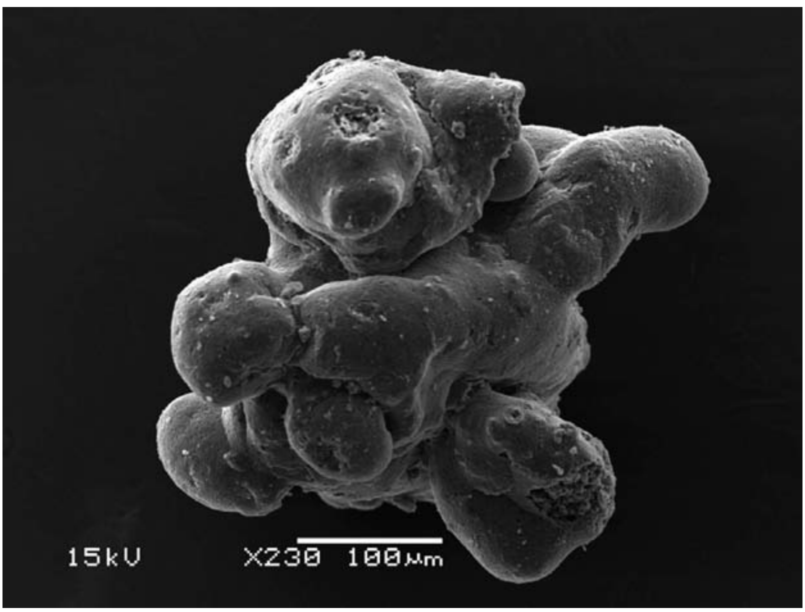


FIGURE 19.10 Spray dried particle showing typical agglomeration.

19.2.1.1.3.5 Drying

Countercurrent spray drying towers are used to dry the droplets and operate with an inlet temperature of ~300°C. The tower design has not changed much over the years; a typical tower outline is shown in the schematic Figure 19.8. The cylindrical section of the diameter is typically in the range 3–10 m. The geometry of the tower around the hot air inlets is dictated by the need to minimize any contact of the hot air with the built up product, and thereby reducing the amount of browning that occurs. This is an important area since higher air temperatures improved thermal efficiency and lead to increased production rates. However, if the distribution is poor, overheating of the powder occurs, leading to potential exothermic runaway and subsequent fires in the tower.

The hot air is generated by an oil- or gas-fired furnace and is uniformly distributed around the tower circumference using a plenum ring. Care must be taken for oil furnaces since poor combustion can lead to black specks entering the tower and causing discoloration of the blown powder. Failure to get a uniform distribution of air or temperature can lead to poor product quality, whereby some granules can be underdried and sticky and some can be overdried and brown. The inlet air can enter radially or with a swirl, that is, some tangential component of velocity. The swirl tends to stabilize the airflow and decrease the exhaust temperature a little, improving thermal efficiency. The exhaust air is ducted out of the top of the tower and any fine product carried over is removed using technologies such as cyclones, bag filters, and electrostatic precipitators.

19.2.1.1.3.6 Cooling and Classification

The powder temperature exiting the tower base is typically over 70°C. This needs to be reduced to allow temperature-sensitive additives to be mixed in. Typically, this is done in an airlift, which transports the powder to the top of the building. A gravity separator is then typically used to disengage the particles from the air. This type of system also performs an initial classification of the powder as large lumps are not transported up the airlift and fine particles do not disengage from the gravity separator. (These fine particles are subsequently removed by a bag filter.) Further classification is often required to remove coarser particles. This is typically done using mechanical screens.

19.2.1.1.4 Operation

19.2.1.1.4.1 Overview: Control and Changeovers

The detergent drying process is a large-scale process, and in modern installations digital control systems are used to control the plant. However, the control of product properties such as density and blown powder moisture tends not to be fully automated, partly due to the multivariable nature of the product properties and lack of robust measurement systems. Therefore, there tends to be a human operator responsible for the starting-up, center lining, and shutting down of the process.

Multiple formulations tend to be run on one tower and with increasing formula numbers, run times for a particular formulation are decreasing. Therefore, the challenge for the tower operators is to quickly bring the system to centerline and acceptable product properties, thereby minimizing the amount of material that has to be recycled back to the slurry.

19.2.1.1.5 Powder Properties

In the majority of granular detergent formulations, the physical properties of the products are determined by the blown powder properties. The key properties are as follows:

Density
Particle size distribution
Cake strength—flow properties
Solubility

Density is typically 250–550 kg/m^3 and determined by many variables such as the formulation, slurry air content, and process conditions. Density is an important quality item since most consumers dose by volume, and therefore, the bulk density is the prime variable to control. Typically, droplets tend to form a skin on the outside as they are dried, leading to the internal water diffusion out of the drop being very slow. In certain cases, this water can turn to steam and expand the droplet causing puffing, and hence, reduced density. The extent to which this can occur will depend on the water content of the slurry, air temperature, and chemical composition. Generally, lower density is caused by a higher slurry water content, higher air temperatures, and a high concentration of film-forming materials. Incorporation of air is also used at high pressures to increase this expansion. However, care must be taken not to overdo this effect since too rapid an expansion can lead to the fracture of the granule and result in an excess of fine material.

An additional factor in bulk density is the ease with which the particles pack. One practice is to spray perfumes and de-dusting agents onto the powder. If these are not absorbed into the granules the liquid can stay on the outside of the particles, leading to poor flow properties and a reduction in bulk density, which is difficult to control.

Particle size distribution. A typical volume-based median particle size is ~400–500 μm. The spread of the distribution is typically wide with some significant fine and coarse powder resulting from the agglomeration process, which takes place within the tower as wet drops collide. Acceptable ends of the spectrum typically range from <5% below 100 μm to <2% above 800 μm. The former is for dustiness of the powder and subsequent dispersion when wet. The latter is to control appearance and dissolution of the powder over time during the washing process.

Cake strength. The cake strength as measured by a uniaxial shear test is often used as a measure of flowability and granule stickiness. These are important properties for both postprocessing and consumer acceptance. The cake strength tends to be an intrinsic function of the formulation and blown powder moisture. Apart from this, the process conditions tend to have only a minor effect.

Solubility. The consumer prefers a fully soluble granule, therefore insoluble residues left by a granule are undesirable. The key factor for solubility tends to be formulation and component interactions, although process conditions can play a role as well. Some of the better-known interactions that can cause insolubles involve sodium silicate—a common ingredient. Poor mixing control with acidic ingredients can result in the production of insoluble silica, and interactions can also occur with zeolite formulations, which will also cause large insolubles. In both cases, careful control of mixing and pH is needed to avoid these problems.

19.2.1.1.5.1 Makeup

One of the common factors that can impact good operation is the attachment of wet slurry to the tower walls, where they dry and form a base for more droplets to stick. This makeup can lead to large lumps inside the tower, reducing thermal efficiency. In the worst case, the makeup near the hot air inlet temperature can result in the overheating of the dried slurry and generate brown and black speckles, which ruin the appearance of the product, leading to shutdown and cleanout. If this is not done, the powder can self-ignite. Makeup is most often caused by poor nozzle positioning and poor airflow control. It is therefore important to ensure these are resolved during the commissioning of a spray drying tower.

19.2.1.1.5.2 Future Developments

As mentioned earlier, the current spray drying process is very well established but is still undergoing constant change and optimization in the drive to reduce costs and increase formulation flexibility and product quality. This is most relevant to the large production units, which make a number of different formulations. As new tools become available, they are applied to these units. Thus, reliability engineering has increased plant utilization, CFD modeling has improved tower airflow control, and process control advances has reduced start-up and shutdown times. Further improvement in modeling capability will allow much better control of product quality and allow the operating windows to be widened in the drive for more cost-effective density and moisture control.

19.2.1.2 Agglomeration in Detergent Processing

19.2.1.2.1 Introduction

Agglomeration is a very widely used process in detergent making. Agglomerators range from high-shear, high-speed mixers to low-shear fluid beds. Processes can range from small-scale batch making to large-scale continuous production. In other words, agglomeration is simply the "sticking together" of smaller particles into some sort of combined entity. This is often not difficult—the real challenge lies in making agglomerates of the desired properties. Agglomeration has been widely used in the last 20 years or so as an alternative to spray drying. Spray drying is well suited for making lower-density particles of more thermally stable materials at high rates. It is most cost effective at high production rates due to the high amount of capital required. Agglomeration is more suited to making higher-density granules at lower volumes and potentially contain more thermally sensitive ingredients. Many detergents are made by combinations of spray dried and agglomerated materials.

19.2.1.2.2 Agglomeration

Agglomeration consists of sticking powder particles with a (liquid) binder. It is possible to agglomerate soft solids where a separate binder is not added, but for this discussion we will restrict the scope to a situation where we have discrete powders and binders. This covers the vast majority of detergent applications. One trite but easily overlooked point is that the use of process aids needs to be minimized for cost reasons, hence, the choice of powders or binders is constrained. Detergent agglomerates include granules where the binder is the active component and levels need to be maximized as well as granules where the powder(s) is the active component and the binder level needs to be minimized.

19.2.1.2.3 Significant Factors in Detergent Agglomeration

Academic research in the last decade has become much more relevant in explaining typical detergent processes. Agglomeration of glass ballotini with dilute glycerol solutions did not provide much help in understanding agglomeration of high or very high viscosity binders often coupled with some chemical/physical change. Agglomeration regime maps in particular are helpful in understanding how the *deformability* of the powder/binder mix and the *degree of saturation* control how the agglomeration proceeds.

This is well covered in a review article by Iveson et al.[1] The agglomeration regime map in Figure 19.11 shows the agglomeration regime as a function of the deformability of the powder: binder system and the degree of saturation.

Deformability (how easily a granule deforms in the mixer). The more deformable the powder: binder mix is in the mixer, easier it is for particles to coalesce and agglomerate on impact due to the viscous dissipation of kinetic energy. The advantage of thinking in terms of

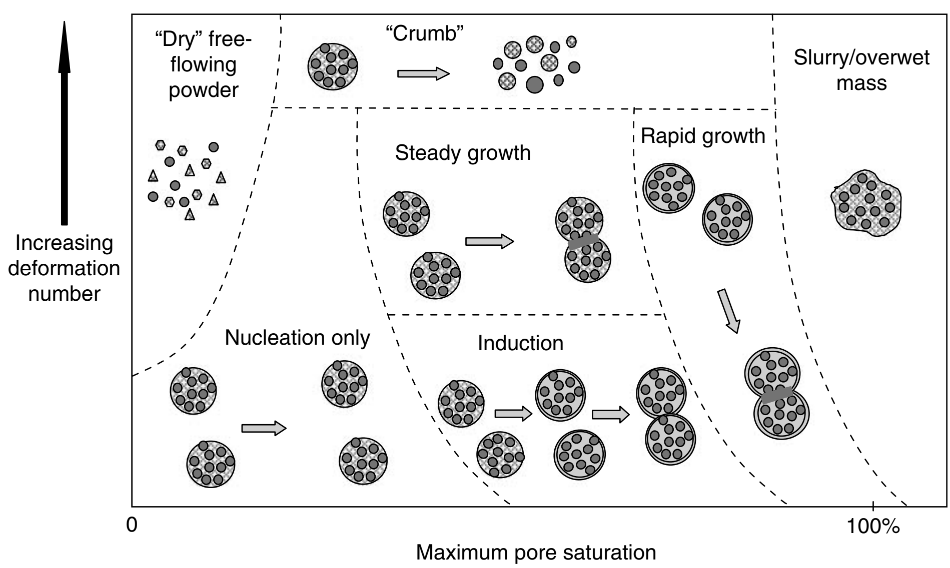


FIGURE 19.11 Phase regime for agglomeration according to Iveson et al.

deformability is that it combines both liquid, powder and process mixing unit properties. Deformability includes a term for the velocity of the collision of two particles and this is controlled by the mixer operation. Focusing on just one component, such as the binder, can be misleading. Nonionic surfactants, which are often low viscosity liquids at ambient conditions, can be successfully agglomerated with a very fine powder such as silica. They cannot be agglomerated with a coarser powder such as sodium carbonate. This is because the very fine powder will make a mix stiffer than the same weight of a coarse powder.

Pore saturation. The more saturated the system is with binder, easier it is for binder to be forced onto the surface during a collision and assist in the coalescence of the particles. If a porous powder is used then the binder can be absorbed *into* the powder and not be on the surface to affect the agglomeration.

One simple way to interpret the map—for a given powder and mixer—is to think of the "*y*"-axis as showing *decreasing* binder viscosity and the "*x*"-axis showing the *amount of binder* added.

Any agglomeration process is a journey around the map. During a batch agglomeration process, we move from left to right as the binder is progressively added. An overwet mass can often be recovered by adding more powder to reduce the effective pore saturation and move the regime from right to left.

$$\text{Maximum pore saturation} \quad S_{max} = w\rho_s(1-\varepsilon_{min})/\rho_l\varepsilon_{min}$$

$$\text{Deformation number} \quad \text{De} = \rho_g U_c^2/2Y_g$$

where

w = mass ratio of liquid to solid
ρ_g = density of granules
ρ_s = density of solid particles
ρ_l = density of liquid
Y_g = dynamic yield stress of granule
ε_{min} = characteristic porosity of the granule
U_c = collision velocity in mixer

19.2.1.2.4 Description of the Agglomeration Regimes

Free-flowing powder. The mix is very easy to deform (i.e., low viscosity binders) and there is not enough binder to form any agglomerates. The mix just looks like the powder.

Crumb. Crumbs are very weak agglomerates that are easily formed and broken. The binder does not have the strength to hold the agglomerate together. As binder levels increase or the mass in further worked we will move directly into the slurry regime.

Slurry or overwet regime. We now have a wet dough.

Nucleation only. We have small agglomerates or cores dispersed in the powder. These small agglomerates have been formed by the initial dispersion of the binder. However, there is not enough binder or the binder is so hard that no further agglomeration will happen.

Induction growth. This region is where the agglomerates are quite hard and have a low tendency to coalesce on impact. Growth is mostly by accretion of powder onto the surface of bigger particles.

Steady growth. The mix is deformable enough and there is enough binder that granules will tend to coalesce and grow.

19.2.1.2.5 Generic Description of a Detergent Agglomeration Process

In any process, some or all of the powders need to be introduced into one or more mixer(s). Some or all of the binder is also introduced into the mixer. The binder needs to be dispersed and contacted with the powders. The higher the viscosity of the binder the harder it is to do this. High-shear choppers need to be used to disperse high viscosity binders. The powder needs to be mixed with the binder and energy inputted to drive the agglomeration process. The granules may need postmaking treatment such as drying and cooling followed by size classification and reblending of the undesired material. This recycle can easily affect the process.

19.2.1.2.6 Factors to Consider in Agglomeration

1. *Initial viscosity of the binder.* This controls dispersion into the powder. Low viscosity binders are easier to disperse. High viscosity binders need mechanical action to break up and disperse them.
2. *Viscosity of the binder in the powder mass.* This may be different to the initial viscosity if the binder undergoes a chemical or physical change such as solidification. It is harder to mix powders into a stiff binder. The higher the binder viscosity the more binder will be needed.
3. *Ability of the binder to "wet" the powder.* Less binder is needed if it does not wet the powder(s) easily. This is easily checked by placing a drop of binder onto the powder(s) and seeing if it disperses into the powder(s). Poor wetting ability is often shown by the binder, which remains as a droplet on the powder surface.
4. *Particle size and particle size distribution of the powders.* Small particles have more ability to coat and stiffen the binder, hence requiring more binder for agglomeration. The most robust agglomerates are made by powders with a wide particle size distribution due to the tighter packing of powder particles occurring in the agglomerate.
5. *"Deformability" of the binder/powder system.* Mixes that are soft and easy to deform agglomerate more rapidly than less deformable mixes. The deformability of an agglomerating mass is a function of the combination of powder properties, especially size, binder properties, and mixer operation (especially speed).
6. *Type and condition of mixer used (high- versus low shear).* The mixer disperses the binder and provides the energy for agglomeration. Understanding the mixer design is important. In particular, "pinch points" where the agglomerating mass is compacted and subjected to high shear can drive the whole agglomeration process.
7. *Chemical/physical reactions during agglomeration.* In a holt-melt agglomeration process, the hot-melt binder typically is of low viscosity initially but immediately starts to harden on contact with the cooler powder. Hence, the deformability of the agglomerating mass is constantly changing.
8. *Amount of recycle required.* Agglomeration processes driven by coalescence of particles will always give a distribution of particle sizes due to the probabilistic nature of the collisions. Hence many agglomeration processes require size classification to give an acceptable final product. The oversize and fines have to be recycled into the system. The recycle of coarse particles back to the mixer can promote further agglomeration and lead to process instability. The recycle of high levels of fines back to the mixer can reduce agglomeration. However, it can be beneficial for stability to recycle some finished agglomerates into the process to act as agglomeration "cores."
9. *Use of dusting.* Fine powder, such as zeolite, can be introduced into a mixer to control the agglomeration process. The powder temporarily coats the surface of the agglomerating particles reducing their tendency to coalesce. Continued mixing reduces this as the dusting layer gets worked into the agglomerates leaving the surface sticky again.
10. *Ambient conditions.* These often seem to be overlooked, but can be very significant. Summer conditions are warmer and more humid than winter conditions. Raw materials will be warmer, and the increased process temperatures will generally increase ease of agglomeration. Increased humidity will affect processes that use aqueous solutions as binders.

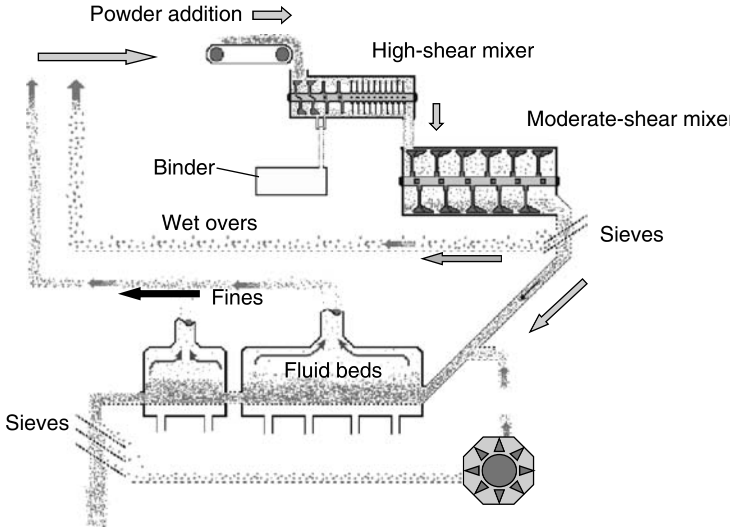


FIGURE 19.12 Schematic of a typical two-stage agglomeration process. (Adapted from Iveson, S., J. Litster, K. Hapgood, B. Ennis, *Powder Technol.*, 117, 3–39, 2001.)

Absolute—when compared to relative—humidity is often more helpful when comparing conditions.

11. *Make-up in the mixer.* Operation of a mixer for extended periods will cause make-up on the sides and tools. If this is extensive, it will tend to increase agglomeration by increasing the mechanical energy introduced into the powder. The frictional heat generated by the mixer will make the granules more deformable. Makeup on tools can disrupt the powder flow pattern. For example, an angled paddle in a paddle mixer will not be able to impart axial motion to the powder if it has excessive make-up. Tool fatigue can occur if tools come into contact with the wall make-up. Finally, makeup will tend to get pulled from walls and become oversized. Although, in some processes the friction from some wall makeup is necessary to help impart the necessary shear to get agglomeration to occur.

19.2.1.2.7 Dense Laundry Process

Figure 19.12 shows a generic description of a two-stage agglomeration process with recycle streams. Generally, the "wet" overs act as agglomeration seeds. The greater the proportion of large, soft particles recycled back to the agglomerator, the smaller the operating window.

19.2.1.2.8 Process Control Strategies

Process control in agglomeration is intended to maintain a consistent granule powder: binder ratio as well as particle size. Raw materials do not have constant properties and all raw material specifications include acceptable ranges whether for purity, particle size or some other quality parameter. Hence, agglomeration conditions alter from batch to batch. Temperature can also vary. Fresh powders can be delivered at high temperatures if the supplier is nearby. Powder feeders do not give completely consistent flow rates but rather oscillate around a set point. In continuous processes, this can be important. The mean residence time in a high-speed continuous mixer can easily be only a few seconds. In this situation, a short "blip" in a powder feeder can completely alter what happens in that mixer. Ambient conditions also change. Finally, so do the operators! One source of variability that is rarely mentioned is the fact that, whatever may be the procedure, different operators operate equipment differently.

Process control alters the degree of agglomeration by altering the deformability of the material in the agglomerator or changing the saturation of the mass. If the degree of agglomeration is too great then the deformability or the saturation needs to be decreased. Options for both batch and continuous processes are as follows:

Reduce the binder : powder ratio.
Make the binder less deformable, for example, cool surfactant pastes.
Make the powder finer, for example, increase the degree of grinding if applicable.
Alter the speed of the mixer.
Altering the binder:powder ratio gives an immediate response but changes the composition of the resulting agglomerate. In systems where there is a drying step, one possibility is to introduce water into the mixer as an additional binder as well as the desired binder. Then the water level can be used to control the degree of agglomeration without altering the final agglomerate composition.

Some processes include an inline-grinding step. In these situations, the degree of grinding or the proportion of the material that is ground can be altered. The finer the particles, the less deformable the agglomerating mass will be and, hence, reduced agglomeration.

Some processes use a fine dusting agent to control agglomeration. This is used mostly in processes where there are multiple mixers.

19.2.1.2.9 Mixer Operation

Mixer operation can provide some process control but not as much as to alter the material. In batch mixers, mixing time and binder addition time can be altered. If an agglomerating mass is more deformable, then the energy input from a mixer can be reduced, for example, by reducing the speed. In horizontal mixers where make-up becomes significant, the speed can often be reduced to reduce agglomeration.

In processes where there are multiple mixers, the addition position of the binder can be varied. For example, one company describes a process that combines a high-speed mixer and a fluid bed agglomerator. The binder—in this case consisting of acidic form of LAS (HLAS)—is introduced into both the mixers, and the proportion of HLAS introduced into each mixer can be altered to control the process. In general, moving binder addition location from the initial to a subsequent mixer will reduce the degree of agglomeration.

19.2.1.2.10 Mixer Operation in Fluidized Bed Agglomeration

In fluid bed agglomerators, spray nozzle height can often be used as a process control tool. This is because the height affects the intensity of the spray flux as well as the time taken for the binder droplets to impact on powder particles. The higher the nozzle is above the fluidized bed, greater the footprint, and hence, lower the spray flux.

If the flux is too low, agglomeration is slow because the amount of binder is insufficient to cause coalescence. In such cases, coating of the particle can occur as the liquid spreads over the particle surface. If the flux is too high, the powder surfaces become overloaded with the binder causing localized excessive agglomeration, often leading to “bogging” of the fluidized bed. The flux is a function of the spraying rate and the nozzle position.

In fluid bed processes where aqueous solutions are sprayed onto a fluidized bed, the spray flux and the position of the nozzles are important. If the addition rate is too low, the binder becomes dried and nonsticky before particles have a chance to coalesce. Hence, agglomeration is reduced. If the spray nozzles are too high above the surface of the fluidized bed, binder droplets can become dried before they hit a powder particle. Again agglomeration is reduced.

19.2.1.2.11 Common Detergent Agglomerate Ingredients

Powders	
Sodium carbonate/bicarbonate/carbonate-containing minerals	Mostly used to neutralize sulfonic acid in "dry neutralization" processes (see Section 19.2.1.2.13 for more details)
Zeolites—especially Types 4A, and X	Fine powder with particles <4 μm. Very useful as an absorbent powder
Phosphate—STPP	Used in some agglomerates. A very good moisture sink, hence, can be used to provide *in situ* drying
Tetra acetyl ethylene diamine (TAED) powder	Commonly used bleach activator. Strong dust explosive. Agglomerated with polymer solutions
Silica	An extremely "absorbent" powder due to its very small size. Can be used to agglomerate liquids or soft solids such as nonionic surfactants. Useful as a dusting aid
Spray dried blown powder	Agglomeration of blown powder can be used to increase bulk density
Sulfate	Used as a filler. High-density, nonabsorbent powder. Will hydrate at <32°C. Used as a "filler" in some agglomeration processes but does not have much influence on the processes
Salt	Used as filler. Does not have much effect on processes
Liquids	
HLAS	Most common and available surfactant globally. HLAS is the acid form of the LAS (see Section 19.2.1.2.13 for more details)
Surfactant pastes, for example, alkyl sulfates and alkyl ethoxylated sulfates	Often very high viscosity, high concentrated solutions
Polymer solutions, for example, polyvinyl pyrolidone, PVOH, polycarboxylates (e.g., Sokalan CP5)	Good binders. Hardening mechanism is by drying
Molten waxy materials, for example, poly ethoxy glycols (PEGs)	Used as hot-melt binders. Hardening mechanism by solidification
Nonionic surfactants	Most of them are very hard to process as liquids at room temperature. No hardening mechanism Agglomerates either need to be very porous and absorbent with nonionic sprayed on or a very fine powder such as silica needs to be used
Silicate solutions	A good polymeric binder. Cheaper than many polymers
Water	Cheap—can be used where the powder contains some soluble binder or can be used as a control tool where other binders are used

19.2.1.2.12 High- and Low-Density Agglomerates and Agglomeration

The bulk density of an agglomerate is a function of its shape, particle size distribution, surface stickiness, and internal porosity. An agglomerate that has a very irregular shape will pack less well than a more rounded agglomerate. Hence, its bulk density will be lower. The internal porosity of an agglomerate is a function of the raw materials and the compaction and working the agglomerate is subjected to during processing.

Fluid bed agglomeration is widely used to give lower-density agglomerates. The low-shear environment of the fluidized bed gives a more open agglomerate structure. In a high-shear mixer, the granules are compacted and this internal porosity is "squeezed out." In addition, granules become rounded resulting in better packing and an increase in density. It is possible to measure a significant decrease in pore size as surfactant agglomerates go through a mixer such as a ploughshare. Low-shear mixers such as fluid beds or drum mixers are used to give lower-density agglomerates. In these cases, the binder needs to be "predispersed" by, for example, a spray nozzle.

In an interesting process, a surfactant is foamed before agglomeration. It is important that the air bubbles in the surfactant are small (preferably <5 m) so that they are retained during processing. One preferred option is to foam a hot-melt surfactant such as an alkyl polyglucoside.

If an agglomerate is very sticky then it will not pack well and result in a low-bulk density. Dusting will result in an increase in density as well as a decrease in stickiness.

The ability of an agglomerate to retain porosity in a mixer is controlled by its deformability. Hence, there is an inverse relationship between the agglomerate deformability and density.

There is no universally agreed definition of what is a high-shear mixer and what is a low-shear mixer. In patent literature, there is universal agreement that high-speed horizontal mixers such as the Lodige CB series are high-shear mixers. Fluid beds and mix drums are low-shear agglomerators. Many mixers have high-speed choppers or dispersion bars to disperse liquids, which can be responsible for inputting much of the total energy. There is no clear agreement for describing such mixers.

19.2.1.2.13 "Dry Neutralization": An In-Depth Discussion

The most common detergent agglomeration process involves the neutralization of linear alkylbenzene sulfonic acid (Figure 19.13) with sodium carbonate or bicarbonate or a combination of the two. LAS is the global "workhorse" surfactant due to its cost and effectiveness. In many regions, it is the only surfactant that is available in quantity. Dry neutralization was the first surfactant agglomeration process. Ironically, HLAS-based processes are probably the most active area of development due to its suitability for use in developing countries and cost advantages in developed countries.

It is to be noted that HLAS—the acid form of the surfactant—is stable. It is a dark, viscous liquid but is easily pumpable at temperatures $>35°C$. It reacts with sodium carbonate/bicarbonate to form the sodium salt and water and carbon dioxide. Sodium LAS is a solid at low water contents, and hence, HLAS can be neutralized and agglomerated with powdered sodium carbonate or carbonate-containing minerals to form a free flowing agglomerate. The lack of water means that no drying step in needed although some cooling step, such as a fluid bed drier, is often required. The equipment required can be simple and cheap, and hence, cost effectiveness is high.

Agglomeration of HLAS with sodium carbonate is actually a complex process due to the changes in the binder properties during the agglomeration. This is best understood by looking at the changes that the binder undergoes. It starts off as a relatively low viscosity liquid, which is (relatively) easily dispersed by a chopper or a dispersion bar or by the powder motion. As soon as the HLAS droplets come into contact with an alkaline surface such as sodium carbonate, the HLAS begins to neutralize to solid LAS. Hence, the deformability of the agglomerating mass decreases with time. As the agglomeration proceeds, there is less and less available carbonate surface to neutralize the HLAS liquid, and hence, the agglomerating mass gets stickier and stickier. The color of the agglomerates gets darker as well due to the unreacted HLAS.

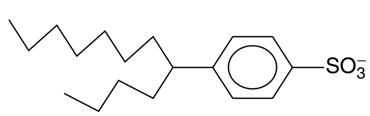


FIGURE 19.13

Practical points about LAS agglomeration by HLAS neutralization:

Owing to the inefficiency of the solid : liquid reaction, a significant excess of carbonate is required to get thorough neutralization. A HLAS:carbonate ratio of 1:2.5 to 1:3.5 is typical. The exact ratio in an agglomerate is a function of the particle size of the carbonate and the available surface area. The ratio of 1:2.5 would apply to ground carbonate. Other powders can be mixed with the carbonate to reduce the amount of carbonate required but can give stickier agglomerates needing additional dusting.

The use of anhydrous carbonate gives higher active agglomerates. This is because the (hydrophobic) HLAS does not wet the hydrated carbonate as well as the anhydrous carbonate. This applies to zeolite as well. Typically, an LAS:carbonate agglomerate could reduce activity from 20 to ~18% due to hydrated powders.

The use of low levels of water in the HLAS (2–5%) speeds up the rate of neutralization dramatically. Levels of water >10% cause the HLAS to gel. A level of 2–3% gives an optimum of increased neutralization without affecting physical properties negatively.

Poorly neutralized agglomerates are stickier and can negatively affect any perfumes that are sprayed on.

The neutralization reaction can take hours to complete. However, the vast bulk of the neutralization takes place in <1 min.

Rapid addition of HLAS can lower the achievable activity as the HLAS has not had time to react.

HLAS-based agglomerates are made in a very wide range of agglomerators.

19.2.1.3 The Finishing of Dry Laundry Detergents

Finishing is the final step in the detergent manufacturing process, whereby all the constituent parts of the detergent product are combined together. This results in the final product that is packed and sold to the consumer.

Finishing generally involves the blending together of some or all of the following dry detergent components into a uniform, homogeneous mix:

Spray dried detergent granules
Surfactant agglomerates
Bleaches and bleach activators
Enzymes
Buffers and fillers
Speciality particles

In addition, various liquid sprays may be applied to the product such as

Perfumes
Nonionic surfactants
Colorants

For smaller operations, finishing can be accomplished in a batch mixer. For larger operations, the use of continuous mixing equipment is more commonly employed.

19.2.1.3.1 Finishing Transformations

Within the mixing unit, the following transformations can commonly occur:

Mixing
Absorption
Heat transfer

Segregation
Agglomeration
Attrition
Solidification

The extent to which any of these transformations occurs is linked to the final product being made, the type of mixer, it's mode of operation (e.g., batch versus continuous) and it's operating conditions (including mixing time).

19.2.1.3.2 Batch Mixing

For relatively small operations, producing <3–5 T/h of final product, batch mixing would normally be selected. In this case, each mix is a discrete batch and care needs to be taken to ensure consistent raw material additions and mixing conditions are applied to each batch (Figure 19.14).

In batch mixing, low-level additives are often preweighed before being added to the mixer. This increases the weighing accuracy and allows multiple small additions to be combined together before dosing into the mixer. High-level additives can also be weighed separately or directly into the mixer using the mixer load cells. For materials that are regularly used (e.g., spray dried granule and sodium carbonate), a feed hopper may be installed above the mixer. When required, material is fed from the hopper into the mixer by a slide gate or rotary valve.

Batch mixing allows a high level of manual operation and low level of automation. It is, therefore, advantageous when starting a new product line or when capital expenditure needs to be controlled. However, accurate records and checklists need to be maintained to ensure all additions are correctly weighed out and added to each batch. With higher investment, a fully automated system can be designed with ingredients added by hoppers using intermediate scales or the mixer load cell. In both cases, care needs to be taken to ensure adequate distribution of low-level ingredients.

Various batch mixers can be used for the final blending of powder detergents. Those commonly used include ribbon blenders, paddle mixers, V-blenders, drum mixers, and ploughshare mixers. Ribbon blenders are of low cost and useful for simple dry mixing operations, which do not require significant liquid additions. In cases where higher levels of liquid sprays are required, a higher level of powder fluidization or free powder surface is required to ensure good liquid distribution. This is the characteristic of the paddle mixer or drum mixer.

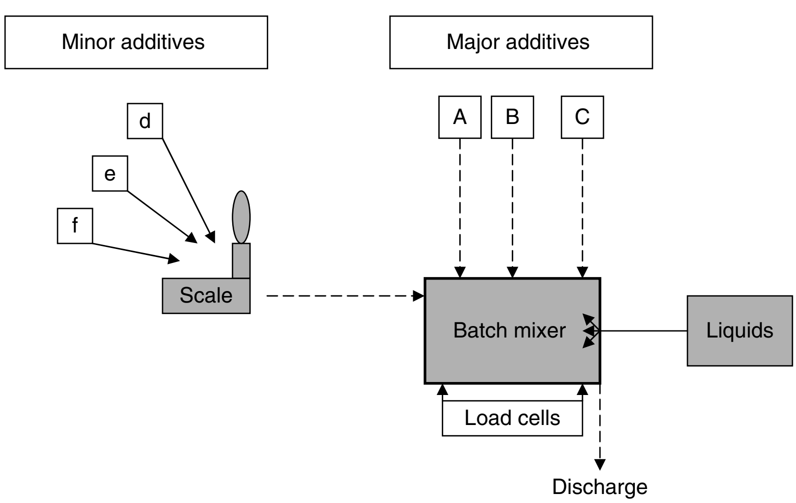


FIGURE 19.14 Batch mixing.

In cases where liquid sprays are added, it is critical that the liquid impinges on powder and not on the walls of the mixer, baffles, or mixing arms. Overspray onto these areas can result in make-up, generation of oversized particles, poor distribution of the liquid ingredient, and poor-quality finished products, as well as frequent shutdowns for cleaning. Liquid spraying should commence only after all the powders have been added to the mixer. The nozzle selection and orientation of the liquid sprays also need to be carefully designed. For common low viscosity liquids (e.g., nonionic, perfume, and colorant solutions), a single fluid (pressure) nozzle should provide sufficient atomization to evenly disperse the liquid into the powder. For higher viscosity materials, two fluid, air atomized nozzles may be used.

The time taken for mixing depends on the design of the mixer. In cases with high fluidization, mixing efficiency is high and mix times can be very short. In such mixers, extended mixing can result in granule breakup and densification, and therefore overmixing needs to be avoided. When assessing the total cycle time of a batch mixer, the following need to be included:

Time for addition of all dry powder raw materials (including time for preweighing of minor ingredients)
Mixing time
Time for all liquid spray-ons
Aging time (if required)
Discharging

After mixing is completed, the batch mixer is completely discharged and is ready for the next batch. Whether the mixer is still running during discharge will be a function of the flow characteristics of the final product and the mixer design. The finished, fully mixed product is collected in bins or other temporary storage containers before quality assurance checks and packing.

19.2.1.3.3 Continuous Mixing

For larger operations, continuous mixing is used. In this case, a continuous feed of all the powder and liquid ingredients is fed to the mixing unit (Figure 19.15).

Upstream processes in the larger detergent manufacturing plants are usually continuous (e.g., spray drying and agglomeration). Their production rates are, however, not always consistent, with some fluctuations in rate occurring over time. To even out these variations, it is common for some buffering to be applied before mixing, often through the use of a surge hopper. Thereafter, these materials and all the other dry powder feeds can be controlled using metered feed systems.

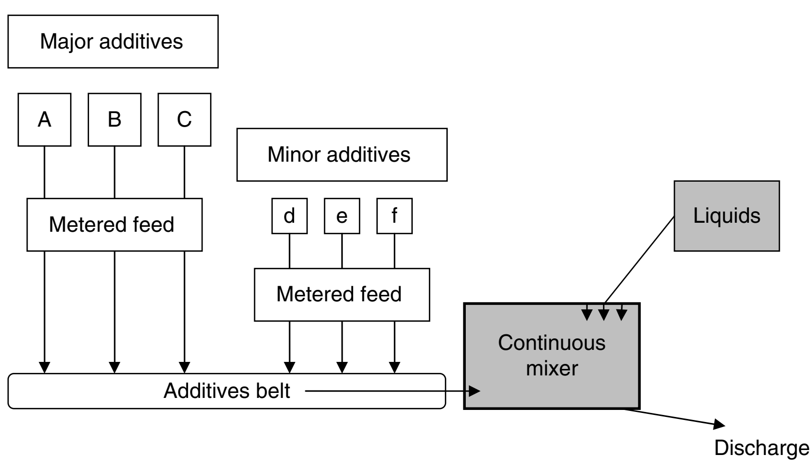


FIGURE 19.15 Continuous process for addition and mixing for additives.

The major ingredient (often the spray dried granule) is often taken as the master additive, with all other addition rates slaved to this material.

The feed systems used vary depending on the nature of the material being fed. For high-level additions of cohesive powders such as agglomerates and spray dried granules, a belt feeder is commonly used. For free flowing, robust ingredients such as carbonate, sulfate, and perborate, a screw feeder can readily be used. Other feeder designs are available and are used for handling specialized materials. In all cases, the feeders either use integrated weighed cells to directly measure addition level or those that have been previously calibrated for the material being fed.

Given that a large number of different dry additives are used in laundry detergents, the number of feed systems in a production plant can be high. To simplify the feeding of all these materials into the mix drum, an additives belt is often installed, which then allows all ingredients to be added on to one belt in a proportional "sandwich" before discharging into the mixer. Usually the bulk ingredients are added first, with the smaller additives layered on top. For operations with multiple additives, a combination of interconnected belts can be used.

A common design of continuous mixer is a rotating cylindrical drum. By adjusting the feed rate, angular rotation speed of the drum, and its inclination to the horizontal, the fill level and residence time can be controlled. As the angular rotation speed is increased, the flow regime in the drum changes accordingly and more turbulent flow is obtained. For good mixing, turbulent flow is required, however, if the drum speed is too high the powder will start to centrifuge and no further mixing occurs. Insertion of baffles within the drum can increase the level of mixing and provide greater turbulence. However, baffles do increase the powder retention in the drum at brand changeover and levels of general make-up.

19.2.1.3.4 Liquid Spray-ons

The drum needs to be sized according to its duty. If high levels of liquid or multiple liquids are to be sprayed on, then a longer drum is required. This not only allows more space to site the spray-on arms, but also provides some time for the powder to *age* (with absorption or solidification of liquids) before discharge. Without *aging*, the risk of powder caking downstream of the mixer can increase.

Liquid sprays need to be sited to avoid adjacent sprays from overlapping. If overlap occurs, it may result in overwetting of the powder surface leading to caking and poor product characteristics. It is also important to ensure that the spray is directed onto the powder and does not impinge on the drum wall. Where spray is on the drum wall, excess make-up can occur in the drum and balling can occur in the final product.

In mixers where multiple sprays are used, the sprays need to be positioned down the drum in a controlled order, with suitable spacing between materials. An *aging* zone should also be included before discharge (Figure 19.16).

Nozzle selection for the liquid sprays is dependent on the nature of the liquid to be sprayed (e.g., its viscosity), the level of liquid required in the final product, how it interacts with the final product,

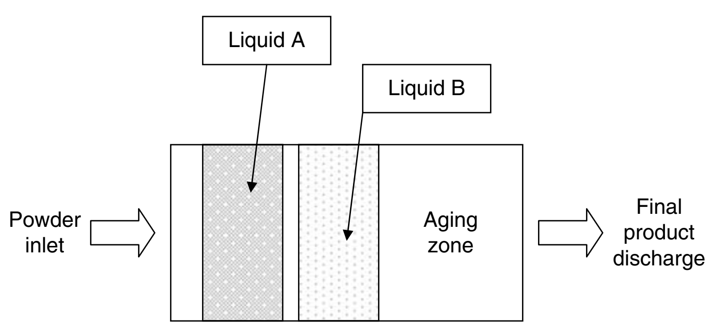


FIGURE 19.16 Liquid spray zones.

and the overall production rate. For low viscosity liquids, (e.g., perfumes, nonionic, and colorant solutions), pressure atomization is normally sufficient. For higher viscosity liquids, it may be necessary to use two fluid, air atomized nozzles to ensure adequate atomization.

Full cone, flat spray, and hollow cone nozzles with a wide range of nozzle angles (e.g., 0–110°) are available. The selection of the nozzle for the given duty will depend on whether full, partial, or selective coverage of the final product by the liquid is required. For instance, where a speckled appearance is required from a colorant spray-on, a narrow angled hollow cone nozzle might be selected. This would only color a proportion of the particles. However, using the same colorant to fully cover the powder, a wide-angled full cone nozzle might be selected. As the nozzle angle increases, or distance between the nozzle and powder bed increases, the risk of spray impinging on the drum wall increases.

19.2.1.3.5 Finished Product Quality

There are a number of aspects that are important during the subsequent handling of the finished product. First, flow properties are important since the product is often stored in bulk containers until the packing lines are available. Second, the stability of the finished product must be tested to ensure that the product quality does not deteriorate on aging. Typical deterioration includes the decomposition of bleach and enzymes, primarily occurring once the bleach decomposes. One of the most stable forms of bleach is sodium perborate monohydrate. This is very stable to temperature, dissolves well, and is also relatively stable to high humidities. It suffers from a cost disadvantage to sodium percarbonate, as well as having boron, which is viewed by environmentalists with concern. Finished products are metastable and can degrade on aging. This is strongly influenced by the amount of water the powder picks up, and therefore, a number of different protection methods are used. Simplest is the poly bag, which is used a lot in developing countries. Here, the moisture barrier properties of the bag provide a reasonable storage life for the product. Cardboard boxes are very common in developed markets. These have inferior moisture barrier properties, and therefore often the board is laminated with polyethylene as a layer between the board to enhance product stability. In addition, the moisture level of the blown powder is usually low to provide some moisture sink for the product again.

Typical problems with respect to aging include caking of the product as well as chemical degradation of the enzymes and bleach, as well as reduction in odor quality as the perfume raw materials react with the bleach or other chemicals in the product.

19.2.1.3.6 Dust Control/Explosion Protection

Raw material feed systems. For materials which are potential sensitizers, (e.g., enzymes), it is advisable to fully enclose the raw material unloading station and feeder system in a booth with dedicated dust control. This ensures that any release of dust is contained. Operators entering the enclosure should do so with appropriate personal protective equipment.

For materials that are potentially dust explosive, nitrogen blanketing can be used for protection against ignition sources. Once diluted within the final product mix, this risk is usually removed.

Mix drum system. To minimize the risk of powder release and protect operators from dust exposure, dust control should be provided on the mixer. This is normally provided at the powder inlet and outlet. Adding the extraction within the mixer is not recommended. This has a tendency to remove excess levels of powders, especially if located near fluidized areas or close to liquid spray-ons.

The spray-on and associated atomization of some liquids (e.g., perfumes) can create an explosive atmosphere. The risk of explosion is low, but to protect the unit and operators the mixer should be equipped with explosion relief panels, water deluge, or some form of commercial dust explosion suppression.

19.3 HEAVY-DUTY LIQUID DETERGENTS

19.3.1 Introduction

HDLs are generally clear, isotropic, homogenous, and thermodynamically stable. These products have only one well-defined, desired state. There are some exceptions to this. Some liquid products and detergents have moved to structured or heterogeneous formulations. These span a wide range of manifestations such as products with dispersed microcrystals to products with suspended particles. For these products, the quality of the product can vary as a result of the process history. Typically, these products are made on the same processes as conventional detergents. Therefore, the rest of this discussion focuses on the production of isotropic products and only touches on the further complications with these other products as appropriate.

With these types of products, much of the burden of the final product quality comes from the choice and control of the formulation. Small changes in key ingredients (e.g., solvents) or impurities (e.g., salts) can make a big difference in the phase behavior of the product leading to poor physical properties, appearance, and stability. Thus, the process engineer and the product designer must work closely together to establish the formulation and insure quality control.

The challenge for the process is to complete the necessary transformations and drive to the thermodynamic equilibrium. The transformations involved are generally not highly complex. Many production units involve only simple hardware and operations. Process complexity comes from demands to make a wide range of products with high efficiency, a large degree of flexibility, and ultimately at high volumes. Although these provide great challenges, they are the elements that drive consumer satisfaction and have fueled the growth of this sector in many markets.

This section provides a broad overview of HDL processing. The discussion begins with the transformational requirements of the product and basic process options followed by market demands and how these affect the choice and design of the process.

19.3.1.1 Transformation Requirements

Production of typical liquid detergents begins with chemical transformations. Many of the more complex chemical reactions are handled during the production of the raw materials, for example, sulfation/sulfonation of anionic surfactants. Chemical transformations in the final production are generally limited to some bulk neutralization and pH adjustment. For example, some materials are supplied in an intermediate, unneutralized form (e.g., HLAS). The biggest concern with these reactions is process control; pH specifications of the finished detergent are near neutral and quite tight to insure product safety and provide an environment conducive to chemical stability of enzymes and other ingredients. The process engineer must also deal with these same chemical stability concerns in process, avoiding in process swings in pH that degrade other materials in the formulation (e.g., alkyl sulfates are susceptible to hydrolysis at extreme pHs). Depending on the formulation, a mixture of cations may be used for neutralization (sodium, calcium, magnesium, etc.) and the process needs to drive the product to the desired, equilibrium salts.

The remainder of the key transformations are related to physical chemistry and state of the product. Here, surfactant-phase transitions can be a particularly important consideration. Anionic surfactants may be supplied in (or converted *in situ* to) a concentrated form in a lamellar, liquid crystalline phase. The final product is typically in a micellar phase. The transition may involve a middle phase that can have a very high, complex rheology and slow phase migration kinetics. Similarly, intermediate compositions can have much higher ingredient concentrations than the finished detergent. For example, water activity and ionic strength can be an order of magnitude different in these intermediates. This can drive unusual phase states that can be difficult to manage. However, these transitional states can provide an environment that enhances the kinetics of difficult transformations such as dissolution of fatty acids (e.g., high temperature and high solvent concentration).

Completion of all these transformations requires just a few basic operations such as metering, mixing, heat transfer, and control. The mixing requirement is generally not very demanding—low to moderate levels only. In fact, heterogeneous products often require limited shear or work input. However, the process control requirements can be quite demanding. Order of addition is important to manage the intermediate states, and pH/stability requirements sometimes drive very tight limits on formula recipe. All these operations can be achieved in either batch or continuous systems. The following section describes each operation and the factors influencing its choice.

19.3.2 Basic Process Options

19.3.2.1 Batch

The simplest and most often utilized process is the batch process. These operations vary in size and complexity. The most basic operation is a simple agitated tank. Additional mixing can be provided by a recirculation loop. The loop can also include a heat exchanger to control the temperature of the batch. The recipe is controlled by several options. For smaller, less sophisticated operations, materials can be weighed and added manually. Larger, more sophisticated operations utilize online weighing/metering. Online systems include mounting the mix vessel on load cells, having separate weigh vessels or totalizing flow meters on the inlet streams. All these options affect the capital- and operating cost of the process. Figure 19.17 shows a typical batch process operation.

The biggest advantages of batch operations are their simplicity and flexibility. These processes can be adapted to the market size and labor costs in the region; they can be very basic, manual operations, or sophisticated, highly automated operations. They can manage a wide range of formulae, orders of addition, and operating conditions at each step. These parameters can be varied almost indefinitely without hardware changes (although there may be an impact to batch cycle time or capacity). Contract or toll processors sometimes use batch operations to make different types of products (e.g., laundry detergent and dish soap) with proper cleanouts.

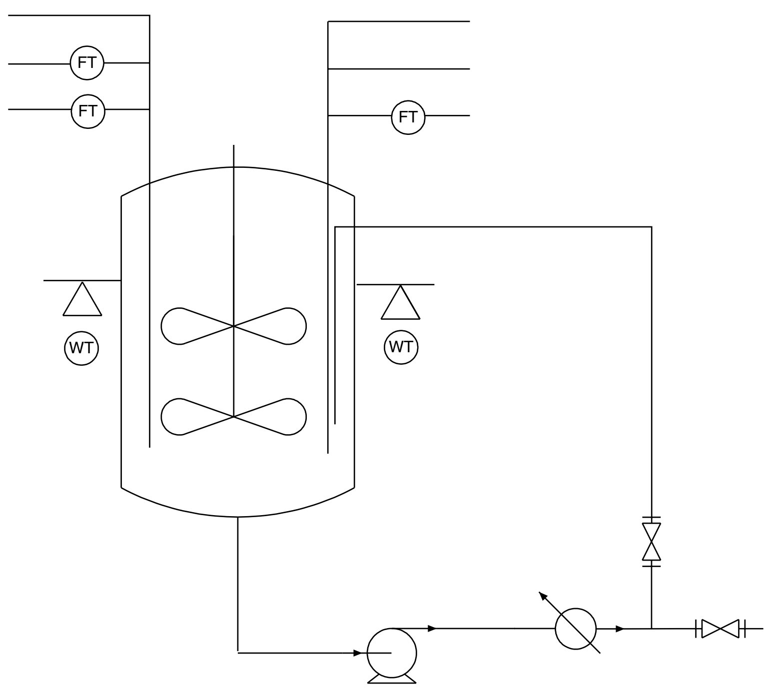


FIGURE 19.17 Typical batch mixing unit.

The biggest disadvantage of batch operations is their fixed scale. Once a batch tank size is chosen, it is difficult to run smaller campaigns. Each weighing/metering approach has a minimum amount that can be added accurately and there is a minimum level that can be properly mixed. There is also some hold up in the batch that cannot be pumped out at the end. This is fixed based on the size of the mixer as well as the hold up volume in the transfer lines to the bottle-filling lines, and therefore, making smaller batches in the same mixer increases the scrap or contamination as a percent of the production.

Similarly, higher volume production is limited by batch cycle times. The batch cycle time is a function of the kinetics of the transformations and transport operations (e.g., how quickly the ingredients and heat can be added and removed from the batch). The engineer can generally manage the residence time it takes to complete a transformation about as well in a batch as any other process. Thus, the unique limitations of batch processing are the transport steps. These tend to be pretty inefficient as all the materials must be moved twice, once in and once out, and both steps use operating time on the mixer.

Along these lines, batch processes offer engineering challenges because they have cyclical demands. For example, a material feed may occur in 1% of the batch cycle time. Thus, the feed rate is 100× what it would be if it were added to a continuous process making the same overall production rate. Similarly, there may be a short step in the batch cycle for cooling. The utility systems must be designed to deliver the entire cooling duty of the batch during that short step.

Finally, the mixing in a batch process can be somewhat limited and variable. Agitators impart a wide range of shear in a large vessel. This is not well suited to handling transformations with critical mixing requirements and is not well suited to high or complex rheologies. Detergent compositions are also subject to aeration during mixing in a batch. Aeration makes it difficult to accurately meter the product, which leads to issues in the packing operation. Disengagement of the air can also lead to separation of a dispersed phase in a heterogeneous (structured) product.

19.3.2.2 Continuous Operations

The alternative to batch operations is a continuous liquids process. These are more sophisticated and more geared to larger-scale operations. They tend to be well suited for complex rheologies and imparting a controlled mixing environment (intense or gentle). A typical process sketch is shown in Figure 19.18.

Depending on the product state and requirements at each point along the process, a number of unit operations can be employed. For mixing, these range from simple inline static mixers (as shown in Figure 19.18) to any of a variety of high-shear mixers. Similarly, heat transfer can be accomplished by a variety of heat exchanger designs including shell and tube and plate and frame-type designs. Here, the choice depends on the rheology of the mixture at that point in the process as well as ease of cleaning.

The biggest advantage of the continuous process is its scale: its ability to be optimized and produce large volumes at relatively low capital. This also implies its biggest disadvantage: lack of flexibility to a wide variety of formulae at low volumes. Generally, wide changes in addition levels or order of addition requires hardware modifications. The size of the process and the product hold up

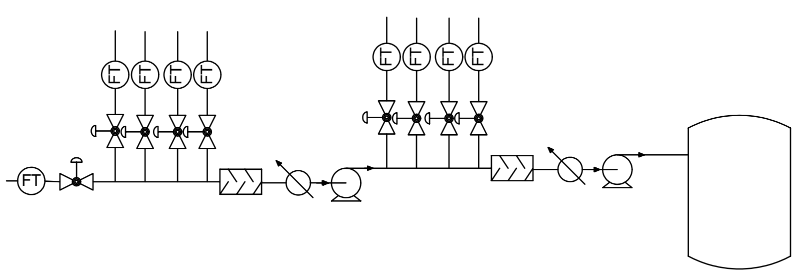


FIGURE 19.18 Schematic of multiple addition points and inline static mixers.

make transitions from one product to another a challenge. The hold up either becomes scrap or off-quality material that must be dealt with. The product quality requirement and economics of scrapping places a practical limit on the minimum campaign or the number of formulae it can handle.

19.3.2.3 Choosing the Optimal Process to Meet Market Demands

In developing markets, either low volume markets or markets where HDL share is low, the manufacturer typically wants to enter the market at a low investment and test the market. At low to modest volumes, basic batch and continuous processes can be relatively inexpensive. However, bulk-handling systems and sophisticated controls can drive up the total capital by several fold. Continuous processes demand more of these by their very nature. Batch systems can be designed to be completely manual and, thus, are often viewed as the lowest capital cost way into low volume production. The cost of labor has to be considered while operating such a process.

To grow a new market or drive a share in existing markets, detergent manufacturers are tending to provide more customized product, tailored to their target consumer. In the past, this meant a few brands with broadly different benefits. Over time, it evolved to the same group of brands with a range of color and scent-based line extensions. In today's world, there is an increasing move to offer a wider range of performance variation to meet the unique needs of consumers better. This approach cascades into a number of demands on the manufacturing operation. First and simply, it means that the process must be able to handle a wider variety of formulations and raw materials.

Second, it means the minimum production campaign must decrease. As the number of variants grows, each new variant is inherently a smaller fraction of the total production. This means that the production campaigns have to get smaller, or the time it takes to cycle through the whole portfolio increases. Larger, less frequent runs translate into higher inventory in the supply chain. This is an important consideration as the cost of carrying inventory can be high. Also, the supply chain will be reacting to the increased number of variants by trying to reduce inventory per variant to keep the total inventory levels constant. In the end, it is quite plausible for a manufacturer to hit their limiting case: where the minimum production campaign makes more product than the target inventory per variant and there will be high financial pressure to make process changes to reduce the size of each campaign.

Another way detergent manufacturers are winning in these situations is by constantly upgrading their lineup of products. This means a more frequent stream of formula changes in manufacturing, which will also increase as the number of variants grows. In all likelihood, the complexity of the upgrades will also increase with more variants because of the wider range in formulations.

On the whole as a market grows, the process must deal with both increasing production and an increasing variety of products. Therefore, the manufacturer is faced with the choice of optimizing on scale (typically with a continuous process) or flexibility (typically with a batch process). Frequently, the process choice is simply the best value process based on the volume and market status at the time of the investment.

19.3.2.4 Late Product Differentiation

Some manufacturers have looked for ways to achieve both scale advantages and support a large portfolio of variants. This can be done with a concept known as late product differentiation. Here, the majority of the ingredients are consolidated in a few base formulations and the bases are then topped off with key differentiating ingredients, dyes, and perfumes. This concept can be used with either batch or continuous processes depending on the application.

Most often, the base-making process is a large-scale continuous operation. The process is lined out on the base: pH, temperature, mixing, etc. are all carefully driven to the target. At the end of the process, the differentiating ingredients are added to make the desired finished product. This final part of the process is designed to be small, easy to line out, and therefore, forgiving to changeovers. With this approach, short runs can be made of each required variant to support a large product lineup and allow a fairly high volume run of the base.

19.3.3 Other Design Considerations

19.3.3.1 Micro

Most liquid detergents are sold in an aqueous solution, and therefore, are subject to the potential for microbial growth. Formulators generally create an environment that is hostile by properly balancing the actives in the formula or adding an antimicrobial agent. Even so, these systems demand good, sanitary designs. The basis for these designs are to avoid stagnant areas (to avoid an area for micro growth), provide good cleanability, and sanitization capability (to eliminate any growth if it occurs). There are standard design techniques and equipment for accomplishing this. The food industry is an excellent source for such information.

19.3.3.2 Recycle

There are a number of sources of off-quality material in any operation, such as process system changeovers, packing system changeovers, process upsets, warehouse, and trade returns. Ideally, all these sources would be eliminated. However, some of these are out of the control of the process engineer and even the manufacturer, therefore complete elimination is often impractical. If material costs are low, the product can be targeted for an alternative use or disposed of. For premium products, the preferred option is to recycle the product to recover its value.

Incorporating recycle into the detergent matrix is not difficult from a transformation point of view. The primary concern is the impact of the recycle on the quality of the new finished product. Of key concern for liquid detergents is managing the impact on physical characteristics such as stability, odor, color, and viscosity. At low levels of recycle, these issues are usually negligible. If the recycle stream gets large, it requires control or management to insure there is no impact to finished product (FP) quality.

19.3.4 Conclusion

The transformations involved in liquid detergent production are generally less technically complex than other detergent forms. Success of the form and the individual producers/marketers has been driven by the pace and volume of new products. Thus, the challenge is in developing a very efficient and agile manufacturing system.

19.4 UNIT DOSE DETERGENT PROCESS TECHNOLOGIES

19.4.1 Introduction

19.4.1.1 Scope of This Section

This section is concerned with detergent-making processes for the manufacture of products in a unit dose form. The sale of household detergents as a unitized dosage has become a significant sector of the market, with all the principal detergent manufacturers offering some products in this form. The most common product type is the tablet form and in recent years this has been joined by products based on a water-soluble film. A broad review of the typical processes used to produce both these types of unit dose is provided in the following sections.

19.4.1.2 Review of the Evolution of Unit Dose Detergent Products

As a preface, it is worth taking a moment to review the evolution of the unit dose form for detergents. It is generally true, and never more so than for unit dose, that the product and process are inexorably linked. Particularly, the physical properties of the desired formulation plays a significant role in determining the suitability of the material for conversion into a unit dose form. It is, therefore, nearly always the case that the product design must evolve through a number of iterations to achieve a suitable balance of product, process, and affordability. The unit dose process development engineer therefore has a unique role to play in delivering the desired consumer experience at an economically viable price.

The desire to sell products as a unit dose originated purely to provide the consumer with enhanced convenience. Measuring by the consumer is eliminated and the potential annoyance associated with dust and spills. In new unit dose forms, additional advantages are being exploited such as the ability to separate incompatible actives. Fabric cleaning detergent tablets were the first unit dose form to appear in the market and the first examples date back to as early as the 1960s when products such as Salvo tablets were sold in the United States. These early detergent tablets suffered from poor rates of dissolution, which contributed to the demise of the form. It was only in the late 1980s before detergent tablets appeared again, and this time, they created a successful segment of the market. By the turn of the century, significant volumes of detergents were being sold in tablet form, a particularly successful segment being for automatic dishwashing tablets. At this time, the unit dose success was limited to Europe, whereas in the United States numerous detergent tablets had failed to create a significant market segment. A recent unit dose development is that of water-soluble pouches, which are typically produced using polyvinyl alcohol (PVOH) film. In Europe, the first launch of this form was for liquid fabric cleaning detergents and later in the United States for automatic dishwashing. The most recent developments using PVOH for automatic dishwashing products have more than one PVOH compartment with different ingredients.

19.4.2 Hard Compressed Tablets

The manufacture of compressed dosage forms (Figure 19.19) for pharmaceutical products has been known for over 200 years and it is this process technology, which has been employed to make by far the vast majority of detergent products in unit dose form. The fundamental aspects of compaction are common to all compacted materials and the tabletting machines used by different industries are also basically similar. The standard steps in uniaxial die compaction are as follows:

1. Flow of the desired amount of powder into the die
2. Application of force
3. Compaction, that is, reduction of voids and increase in bulk density and bond formation
4. Removal of force
5. Ejection of the tablet

Figure 19.20 shows a typical strain curve for the compaction cycle as a function of stress. In principle, it would be possible to predict quantitatively the mechanisms from the physical and chemical properties of the powders and the applied forces. In reality, this is not yet feasible.

The initial powder density in the die will depend on the particle size distribution and particle shape but for many powders it is likely to be about 50% of the intrinsic density. After the application

FIGURE 19.19

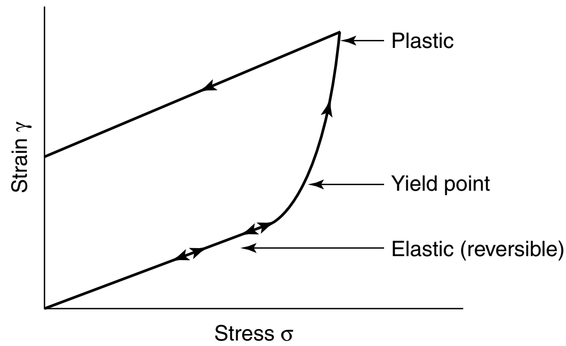


FIGURE 19.20 Typical strain curve as function of stress.

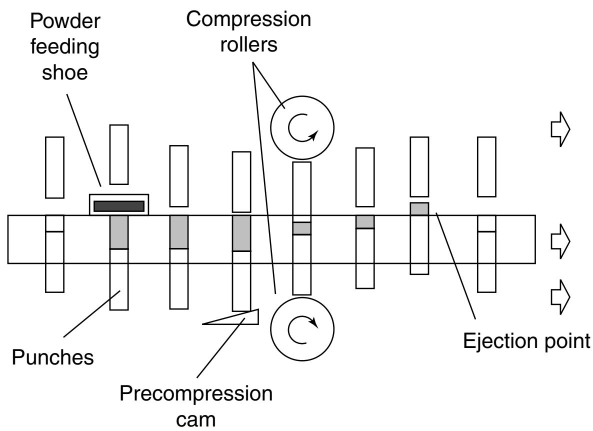


FIGURE 19.21 Cycle of a rotary tablet.

and removal of the compressive force, the average density would have increased to ~85% of the maximum. However, for most laundry tablets it is a lot less due to the need for very rapid dissolution.

During compression within a die, there are a multitude of physical and mechanical processes occurring. These include powder flow, percolation, friction, lubrication, fracture, elastic, viscous, and plastic deformation. As a result of these transformations, a powder is converted into a tablet in a matter of some few hundred milliseconds.

The stages of a typical production rotary tablet press are shown diagrammatically in Figure 19.21.

In developing a detergent tablet, the key concerns for the process engineer is to achieve the optimum balance of strength to dissolution. Tablet strength is important for packing operations in the plant and subsequent distribution to the trade and dissolution is critical for the performance of the product and to avoid highly undesirable product residues at the end of the wash. In addition, there are also a number of less obvious factors to be considered such as

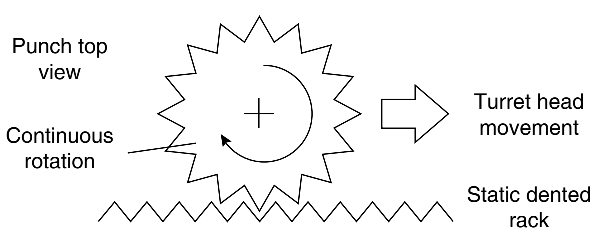
Powder flow ability. To achieve a consistent weight, it is important that the feed powder has consistent flow properties. Older presses often use purely gravity-based feed systems, whereas more modern presses may have assisted feed systems with features such as rotary paddles in the feeding shoe. The assessment and factors influencing powder flow are well documented in the literature, but for tabletting the final test must be on the production scale press.

Compression properties. The compressibility of the desired actives is unlikely to be suitable without some modifications. The compressibility of each ingredient can be significantly modified by adjusting particle size distribution and porosity. Typically narrow, fine particle size distribution (PSDs) require high forces and produce a tablet with low porosity and, therefore, poor solubility. Granular PSDs, produced by processes such as agglomeration or spray drying are much more suitable for tabletting. During the production of pharmaceutical tablets, the raw materials are always pretreated by a batch granulation (agglomeration) process for this reason. In addition, additives may be used to improve both solubility (disintegration) and tablet strength. Disintegrants work by either swelling on contact with water to break apart the tablet or they are themselves very soluble. Binders are generally "sticky" deformable materials, which will act to stick together the less deformable active ingredients. This facilitates the production of either harder tablets at the same compression force or improved disintegration rates for the same hardness produced at a lower compression force.

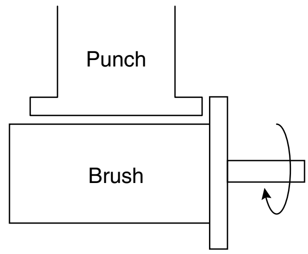
Punch sticking. Typical detergent formulations are often quite cohesive compared to many pharmaceutical formulations. The result is that the product sticks to the upper punch of the press. The problem is restricted to the upper punch since this punch leaves the product with a vertical movement while the tablet leaves the lower punch with a shearing force at ejection. The result is that the powder very rarely remains on the lower punch. Punch sticking is a major problem in production for both product quality and production reliability causing frequent shutdowns for cleaning. Adjusting the formulation is one approach to solving this problem but one generally has limited degrees of freedom in this respect. The problem is generally solved by the process design. Four common options are described in the following:

Punch coatings need to be tested by trial and error. Options range from polished chrome plate to Teflon.

Continuous twist system in both punches in the precompression and compression phases.



Cleaning brushes to remove makeup from the punches. It is very important to place close attention to the means for removing the brushed off powder to avoid accumulation of powder within the press using this approach.



Liquid spray to bring antiadhesive silicon oil to the surface of the punches (top and bottom). The oil is sprayed during a few seconds several times during the day. Magnesium stearate powder is also used for the same purpose.

The process/quality control strategy for the manufacture of detergent tablets is largely based on the approach developed for pharmaceutical tablets. The tablet weight is controlled by the fill cam position. In modern presses, this will be a motorized adjustment and is linked by a feedback control loop based on the compression force. Typically, this can achieve a weight variation of less than +/− 4% (three relative standard deviations), since for a given material the compression force is linked to slight changes in the powder density. In recent years, some press vendors are also offering systems that periodically sample and automatically weigh tablets.

One enhancement of the tablet press is the capability to make multilayer tablets. This option was developed some decades ago for pharmaceutical tablets and it is now often seen in automatic dishwashing tablets. The multiple layers are achieved by simply replicating the fill/compression stations on the press. Hence, the sequence for a two-layer tablet would be fill layer 1/compress/fill layer 2/compress/eject. To achieve a good bonding between the layers, the final compression is always at the highest force.

Since the hard compressed technology has been much developed for pharmaceuticals, production systems based on this approach are likely to run at high process reliabilities (>80%).

19.4.3 Soft Compressed Tablets

For some applications, such as laundry tablets in front-loading washing machines, the requirements for tablet dissolution are extremely demanding due to the low wash temperature, low agitation, and short wash times. In this application, some detergent manufacturers produce very weak tablets that are able to disintegrate very rapidly. The problem with this approach is that the tablet is too weak and sustains significant damage in the packing operations and shipment to the trade. One solution to this problem is to coat the tablet to boost the strength while still maintaining very quick disintegration. The application of the coating is typically performed while the tablets are passed along some form of perforated conveyor belt using a spray or liquid “curtain” method. Standard pharmaceutical drum-coating methods are not suitable since the tablets are too big and too weak.

To give some perspective as to the magnitude of the difference between “hard” and “soft” compressed tablets, typical hard detergent tablets (such as those produced for automatic dish washing) are compressed at pressures over 40,000 kN/m^2, whereas “soft” tablets use pressure as low as 2,000 kN/m^2.

An additional problem that is often much more significant with soft compression tablets is that of material sticking to the upper punch. This is more common with the production of weak tablets since the bonding forces between the particles themselves and those between particles and the punch surface are of a similar magnitude, and hence, some powder is likely to remain on the surface of the upper punch when it pulls up before ejection. Potential solutions to this problem include those mentioned earlier for hard-pressed tablets, one of the best options being the twisting punch. Unfortunately, a twisting punch will not work if the tablet is not circular! An alternative approach is to use single-sided tablet presses that have an upper compression plate instead of a punch. This plate can rotate thereby minimizing sticking. This type of tablet press is also commonly used for the production of stock cubes for cooking where the ingredients are very sticky. The principals of a typical single-sided press are shown in Figure 19.22.

All the considerations described earlier for hard-compressed tablets apply to soft tablets but it is evident due to the nature of the “weak” tablet that some concerns may be more problematic. In particular, the generation of dust in the environment of the press can be a big production problem. If the removal of the dust is not addressed, over time, it will lead to a reduction in process reliability. Although it is not impossible to achieve high process reliabilities, it is certainly more challenging and requires a high degree of attention to the details of all aspects of the press design and upstream and downstream integration with the powder feeding and packing operations.

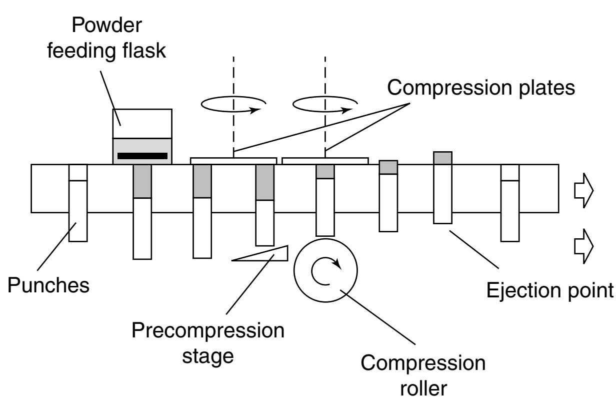


FIGURE 19.22 Schematic of tablet making process (direction right to left).

19.4.4 Water-Soluble Pouches

19.4.4.1 Single Compartment

Compressed tablets have the obvious disadvantage of only being able to deliver as much liquid as may be absorbed within the powder. This is typically <10% w/w. Driven by the same advantages of the solid unit dose form, a number of detergent manufacturers have developed unitizing processes that can handle liquids. These products are all based on using polyvinyl alcohol (PVOH)-based films. PVOH is a good choice since it has good mechanical properties for pouch-forming processes, has reasonably rapid solubility in water, and is available in commercial quantities at a price that is consistent with detergent products (Figure 19.23).

19.4.4.1.1 Vertical Forming Processes

The first versions of liquid-filled PVOH pouches used a common existing process technology called vertical form fill seal (VFFS). This technology (Figure 19.24) was well established and employed on a wide range of products from tea bags to large bags of detergent powders. The disadvantage of

FIGURE 19.23

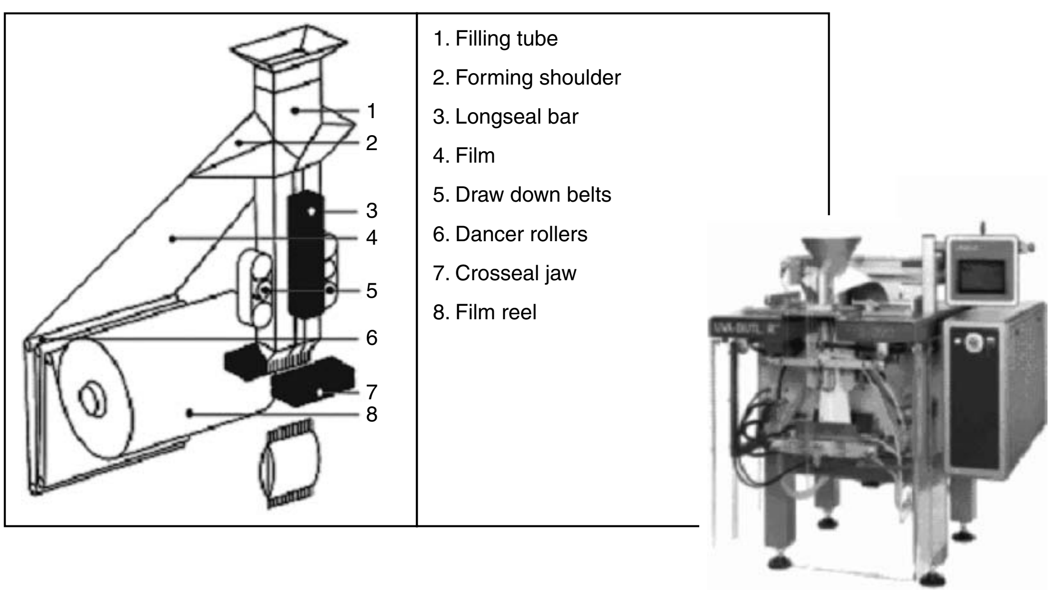


FIGURE 19.24 Schematic of film path.

this process is that it is quite capital intensive for the large outputs required for detergent unit dose products and consequently the profitability was generally poor. This is due to the fact that only one pouch is made at a time. In addition, as can be seen from Figure 19.24, this process is essentially a continuous folding of the film. Since it is impractical to fill the so-formed pouch 100%, and since the film is not under tension, the resultant product is quite flexible or "floppy." It was found that the majority of consumers did not like this floppy appearance.

19.4.4.1.2 Horizontal Forming Processes

As a natural evolution from the VFFS process, manufacturers of PVOH pouches have moved production lines to more efficient processes based on equipment, making more than one pouch at a time. These are often referred to as multilane converters. This technology is a development that is based on packaging technology in which deformable film materials are formed into multiple moulds to produce packages. This type of process is most often run in an horizontal mode although there are examples where the same principles are applied to a rotary cylindrical design. An example which will be familiar to the reader is that of prepacked sandwiches, here the semi-rigid part containing the sandwich is produced using the horizontal principle. PVOH pouches may be produced on this type of equipment using the following steps:

PVOH film, from a roll, is accurately positioned above a set of moulds having the desired size of the final product.
A combination of vacuum and heat is used to draw the film into the mould.
The product (liquid or powder) is dosed into the mould.
A second roll of PVOH film is applied to the top surface of the mould.
A suitable combination of heat and pressure is applied to seal the second film to the top surface of the first film.
The set of pouches are cut along the seal lines to form individual pouches.
The pouches are finally ejected from the moulds.

In addition to improving the capital efficiency compared to the VFFS process, the horizontal forming process involves creating some tension in the film, which will at least partially relax postprocessing. This results in a product with a neat, more rigid appearance, which is preferred by most consumers. Although the process may appear simple from the preceding description, this is still a relatively new venture for the detergent manufacturers and the equipment vendors, there being many details of the process that require careful attention to produce a consistent output at high process reliabilities.

PVOH film quality. If the product is to contain a liquid, it is vital that a high-quality source of film is used. Prior uses of PVOH film were less sensitive to small defects in the film, and therefore, it will probably be necessary to work closely with your film supplier to ensure that your quality requirements are clearly understood.

Weight control. Compared to the tabletting process, this process is less flexible with regard to weight control since the "mould" is fixed. This is typically not an issue for liquid products since the density is very consistent, however for powder, fluctuations in the powder density will result in changes in the powder weight in each pouch. For the process engineer, this must be addressed by upstream control of the powder-making process and in trying to maintain very consistent conditions on the pouch-making line. However, it is very unlikely that the high degree of weight control achievable on a tablet press can be reproduced by this type of process.

Leaker detection. If the product is a liquid, then leaking pouches caused by poor sealing or film quality must be detected as soon as possible. For the consumer, it is clearly imperative to avoid a shipping product where some pouches are leaking and in production, leakers can cause major downtime problems. For example, if liquid gets into the vacuum system this can result in significant lost time to cleanout and if the vacuum pump is not protected by a "catch pot" it can even result in the destruction of an expensive vacuum pump.

The production of water-soluble pouches has many similarities with high-speed packing lines such as those used to produce disposable nappies (diapers), and the process engineer working in this field would do well to visit such types of production facilities to compare their approaches to quality control and process optimization. Here, we are talking about aspects ranging from high-speed vision systems for product inspection to high-accuracy servo drive motor systems to ensure reproducible and highly accurate process manipulations.

For comparative output to a tabletting line, the capital cost is higher and the process reliability is likely to be lower. This is not an inherent limitation of this technology but is rather a reflection of the relative infancy compared to tabletting.

19.4.4.2 Dual and Multicompartment

As the market for detergents in PVOH pouches became somewhat established, leading manufacturers developed more complex products as a means to differentiate their product from others in this very competitive market. Two prime examples are P&G's Cascade ActionPacs®/Fairy Active Bursts (Figure 19.25) and Reckitt Benckiser's Finish Quantum® (Figure 19.26).

19.4.4.2.1 Horizontal Forming Processes

The horizontal forming process for PVOH pouches can be adapted to produce pouches with more than one section or compartment. For obvious reasons, precise details are proprietary to each manufacturer; however, it is evident from the product itself as to the basic principles employed.

19.4.4.2.2 Moulding Processes

A relatively recent development for unit dose products based on PVOH is a process based on injection moulding. This is generally a very common and well-known process for products ranging from plastic automotive parts to children's toys.

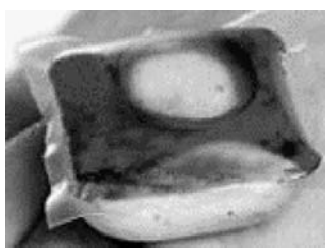


FIGURE 19.25 Version of dishwashing unit dose.

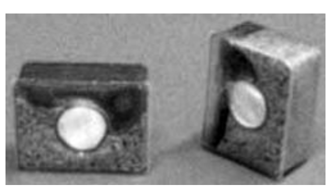


FIGURE 19.26 Another version of dishwashing unit dose.

The advantage of injection moulding is that quite complex shapes can be easily produced, provided that the injection material can be made to flow into the mould. For the application to unit dose detergents, there are two principle challenges to be addressed by the process development engineer who desires to employ this process for PVOH unit dose detergents. First, formulating a PVOH mix that is conducive to injection moulding. PVOH alone will not be suitable and therefore additives that do not adversely effect the desired final product properties of the PVOH such as its ability to dissolve rapidly must be found. Second, the complexities of dosing multiple ingredients into the injection-moulded PVOH part at viable production line speeds without contamination from one to the other. The existence of such a product in the market demonstrates that these challenges can be solved.

19.4.4.2.3 Recycle Considerations

In the manufacture of traditional nonunit dose detergents, the recycle or "reblend" of an off-specification product was an important necessity for both environmental and economic considerations but it was not an area of the process that required complex process innovation. A box of powder or a bottle of liquid may be simply opened and added back to normal production at a low level. Even with the introduction of tablets, this did not create significant difficulties since tablets are easily converted back to powder in a grinder ready for addition back to the production of fresh powder.

Conversely, with the introduction of water-soluble unit dose pouches, the recycle question immediately became much more complex. It is an inherent element of these processes (except the VFFS) that the production of pouches results in a side edge trim being the outer edges of the film, which is held during the process to ensure that the web of film is under positive control. This may only be a few percent of the total film used but nevertheless, it must either be scrapped or returned to the film producer for reblending. A more complex challenge is the difficulty in dealing with off-specification pouches since there is no immediately obvious means to recover the product separately from the film. The pouches could be cut open in some type of knife mill but it is not easy to cleanly separate the film from the active product. The challenge becomes even more difficult for the new dual compartment pouches containing powder and liquid.

19.4.5 Summary and Trends

The last decade has seen an explosion of unit dose product forms in the household detergent market. It is still most popular in Europe where some segments have passed the 50% mark for unit dose such as automatic dish washing in Germany where unit dose accounts for more than 60% of the market. Fast-moving consumer goods are a very competitive market, and in a very established area such as detergents, unit dose has become the prime vehicle for manufacturers to seek to establish competitive advantage and to be seen at the leading edge of innovation. This trend, driven by marketing, has created a very exciting environment for the process development engineer working in this field—the technical challenges of unit dose being in addition to those related to the production of the base powder or liquid.

Since the launch of the first simple tablets, the unit dose form has become more complex almost every year thereafter. Some of them include dual layer tablets, tablets with inserts, and, recently, the multicompartment PVOH pouches. The need to remain competitive will continue to drive more complex forms of unit dose products for the foreseeable future.

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