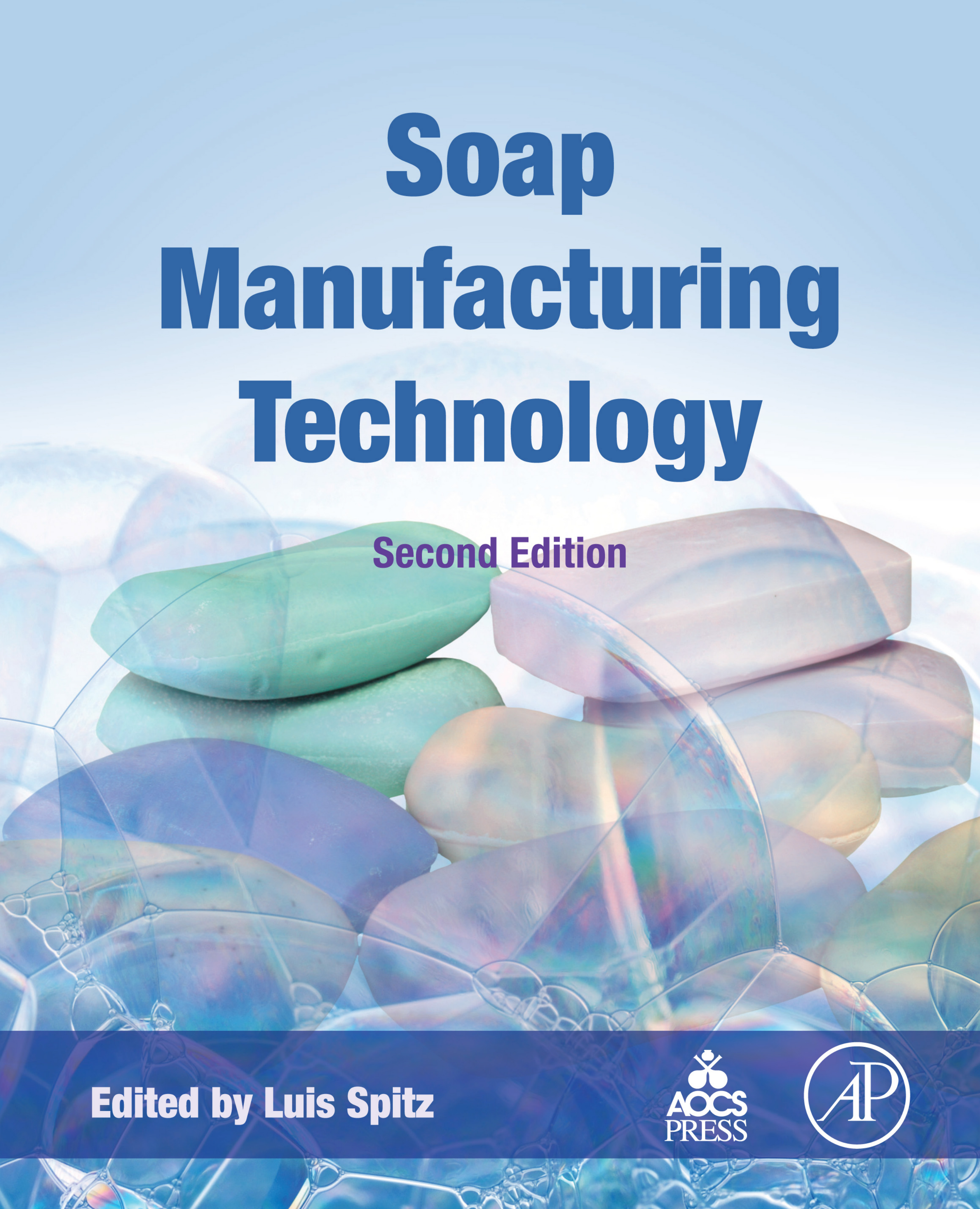
Soap Manufacturing Technology

Second Edition



Edited by Luis Spitz

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Editor

Luis Spitz

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Preface

This publication completes a 25-year-long soap book journey. It started in 1990 with *Soap Technology for the 1990s,* followed by *Soaps and Detergents: A Theoretical and Practical Review* in 1996, *SODEOPEC—Soaps, Detergents, Oleochemicals and Personal Care Products* in 2004, and *Soap Manufacturing Technology, First Edition* in 2009.

I extend my gratitude to the entire AOCS Organization, to the AOCS Press staff for all of their help and hard work.

My appreciation to all the contributors who shared their knowledge in many important subjects. Their contribution benefited all of us.

It has been a most interesting and satisfying "bubbly journey."

I also salute everyone that has shared my passion for the world of soaps, its interesting history and its importance in health and beauty applications.

Luis Spitz

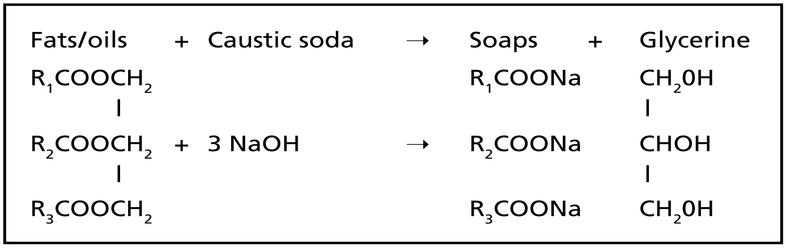
1 Implications of Soap Structure for Formulation and User Properties

Norman Hall
Continua Consulting Service, United Kingdom

Basic Chemistry

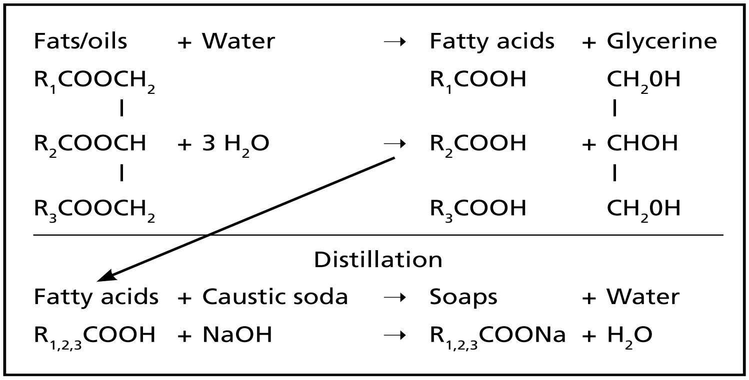
The fundamental principles of soap composition and performance are generic and apply to all soaps. The chemistry of soapmaking is very simple. Soaps are the salts of (mainly) saturated and unsaturated fatty acids having carbon number C10 to C18. The source of the fatty acids is always a blend of natural triglyceride oils. However, relatively few manufacturers make soap by neutralizing a blend of fatty acids. Most create soap directly from the blend of oils.

To make soap directly from oil, a blend of glyceride oils is reacted with a strong sodium hydroxide solution to give the soap, plus glycerine—and a lot of heat. Separating the soap from the glycerine byproduct is not easy, and may not even be necessary.



$$\begin{array}{lllllll}
\text{Fats/oils} & + & \text{Caustic soda} & \rightarrow & \text{Soaps} & + & \text{Glycerine}\\
R_1COOCH_2 & & & & R_1COONa & & CH_20H\\
\quad | & & & & & & |\\
R_2COOCH_2 & + & 3\ NaOH & \rightarrow & R_2COONa & & CHOH\\
\quad | & & & & & & |\\
R_3COOCH_2 & & & & R_3COONa & & CH_20H
\end{array}$$

The alternative is to split the triglyceride oil into fatty acids and glycerine using high temperatures and high pressures. In this case the fatty acids and glycerine can easily be separated. The separated fatty acids are normally distilled, blended, and then neutralized with NaOH solution to form soap.

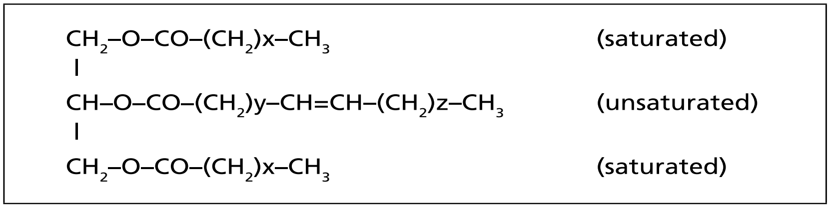


$$\begin{array}{llllll}
\text{Fats/oils} & + \text{ Water} & \rightarrow & \text{Fatty acids} & + & \text{Glycerine}\\
R_1COOCH_2 & & & R_1COOH & & CH_20H\\
\quad | & & & & & |\\
R_2COOCH & + 3\ H_2O & \rightarrow & R_2COOH & + & CHOH\\
\quad | & & & & & |\\
R_3COOCH_2 & & & R_3COOH & & CH_20H\\
\hline
 & & \text{Distillation} & & & \\
\text{Fatty acids} & + \text{ Caustic soda} & \rightarrow & \text{Soaps} & + & \text{Water}\\
R_{1,2,3}COOH & + NaOH & \rightarrow & R_{1,2,3}COONa & + & H_2O
\end{array}$$

Whether it is better to make soap by classical saponification or by a fatty acids route involves economics, supply chain issues, raw material, and finished product qualities. The availability of equipment and of operators skilled in the relevant processes can be important issues to consider.

Glycerides

The alkyl chains R_1, R_2, and R_3 on the triglyceride molecule of the oil or fat include both saturated and unsaturated fatty acid types, of different carbon atom chain lengths (carbon numbers), for example:



$$\begin{array}{ll}
CH_2\text{–}O\text{–}CO\text{–}(CH_2)x\text{–}CH_3 & \text{(saturated)} \\
| & \\
CH\text{–}O\text{–}CO\text{–}(CH_2)y\text{–}CH{=}CH\text{–}(CH_2)z\text{–}CH_3 & \text{(unsaturated)} \\
| & \\
CH_2\text{–}O\text{–}CO\text{–}(CH_2)x\text{–}CH_3 & \text{(saturated)}
\end{array}$$

This example shows a triglyceride with two saturated fatty acid chains (say, palmitic acid, C16) and one unsaturated fatty acid chain (say, oleic acid, C18:1). Several different combinations of saturation/unsaturation and chain length are possible on a given glycerine backbone, resulting in oils that differ widely in their characteristics—especially their melting points. These differences are very important for edible applications, where the oils are used as triglycerides, but are much less important for soap applications, because in soapmaking all the fatty acid chains are separated from the glycerine backbone.

For soaps the only important factors are the relative proportions of saturated to unsaturated fatty acids (measured by the *iodine value*—the grams of iodine reacting with the unsaturated component in 100 g of oil or fat), and the lengths of the fatty acid chains (carbon number).

The proportions of saturated and unsaturated fatty acids and the chain lengths of those acids are characteristics of the oil or oil blend used for making soap.

Why Use a Mixture of Oils?

A blend of oils is almost always used to make toilet soaps or laundry soaps. The most common oils are coconut oil (CNO) or palm kernel oil (PKO), which, understandably, are generally called nut oils, and tallows (AT or T) or palm oils (PO), which are generally called non-nut oils. To get the best performance from soaps, you need both nut oils and non-nut oils.

The Non-Nut Oils (Tallows or Palm Oils)

These oils provide long-chain-length saturated fatty acids (C16/C18—palmitic and stearic acids), resulting in soaps that are almost insoluble at normal user temperatures and therefore do not lather. To put this insolubility into context, consider that calcite is more soluble in water at 25 °C than is sodium stearate. However, these almost insoluble soaps add to lather stability and add hardness, which makes the soap solid.

Lather stability is to a large extent governed by the rate at which a liquid film drains under gravity from between the bubbles. When the liquid film becomes so thin at any point that the film sides touch, then the bubbles burst. Any mechanism that slows the rate of liquid drainage will increase lather stability.

When the liquid film contains insoluble particles, these can sometimes “bridge” the film sides and cause premature lather instability. This can happen with very large particles of filler materials. However, the particles of insoluble soaps are very small, and they are asymmetric. There are two consequences of this asymmetry.

First, in the same way that sticks of wood flowing in a fast-moving river will align with their longest axis parallel to the river flow, so the insoluble, asymmetric particles of sodium stearate and sodium palmitate will align so that their long axis is parallel to the flow of liquid draining from between the bubbles of lather. The narrow axis of the stearate/palmitate particles is very small, so it is unlikely that the particles will bridge the film sides until most of the liquid has drained.

Second, and most important, at the junctions between the air bubbles there is a region of much slower liquid flow. This is the Gibbs-Plateau border. In this region, motion of the particles of sodium stearate/palmitate become much more random, like wooden sticks floating randomly in a slow-moving pond of water.

Just as sticks floating in a slow pond can cause a log jam that inhibits the water flow, so the particles of sodium stearate/palmitate can collect in the the Gibbs-Plateau border to an extent that they will block the flow of liquid draining from the lather. This increases the time it takes for the bubble film sides to touch and for the bubbles to burst—and so increases lather stability

Tallow or palm oils also provide long-chain-length unsaturated fatty acids (mainly C18:1), and the chain length gives soaps with reasonable solubility but only moderate lather stability and rather poor lather volume. However, the moderate lather stability of sodium oleate from tallow or palm oils is improved significantly by the lather-stabilizing effect of the insoluble sodium stearate/palmitate soaps provided by the same oils. This means tallow soap or palm oil soap alone can give a reasonable amount of lather and have good lather stability, provided the use temperature is high enough (over 25–30 °C) to dissolve the sodium oleate.

The Nut Oils

These oils provide short-chain-length fatty acids (especially C12, lauric acid) that result in soaps of moderate solubility, but with high lather when they are dissolved. Solubility can be increased by using the soap at a higher temperature, but sodium laurate does not dissolve significantly until the temperature is over 40 °C.

The Importance of the Oleate:Laurate Eutectic Mixture

It is a common but mistaken idea that nut oils make soap lather because the C12 soap has a high lather. It is true that C12 soap has a higher lather than C18 soap (which effectively does not lather at all) and a higher lather than C18:1 soap. However, the lather of a soap containing both tallow/palm and nut oil is much higher than that of C12 soap alone. The reason for this is fundamental to many aspects of the performance of soap tablets.

When a system contains both C12 and C18:1 fatty acid soaps together, the mixture has a solubility that is much higher than the solubilities of either of the individual components. For example, a 1:1 mixture of C12 sodium soap and C18:1 sodium soap is very soluble and has a very high lather. This mixture will also make the soap softer. Consider the Krafft temperatures (T_k) of

Sodium C12 soap (sodium laurate) = 42 °C
Sodium C18:1 soap (sodium oleate) = 28 °C

The Krafft temperature is the temperature, or more precisely the narrow temperature range, above which the solubility of a surfactant increases rapidly. At this temperature the solubility becomes equal to the critical micelle concentration. When micelles form in the solution, the detergent can dissolve in the micelles more easily than in the water, and the solubility increases rapidly.

However, the Krafft temperature of the sodium oleate/sodium laurate 1:1 mixture is below 0 °C, which means it is very soluble even in cold wash water, and so it lathers quickly and gives a good amount of lather (see Figure 1.1).

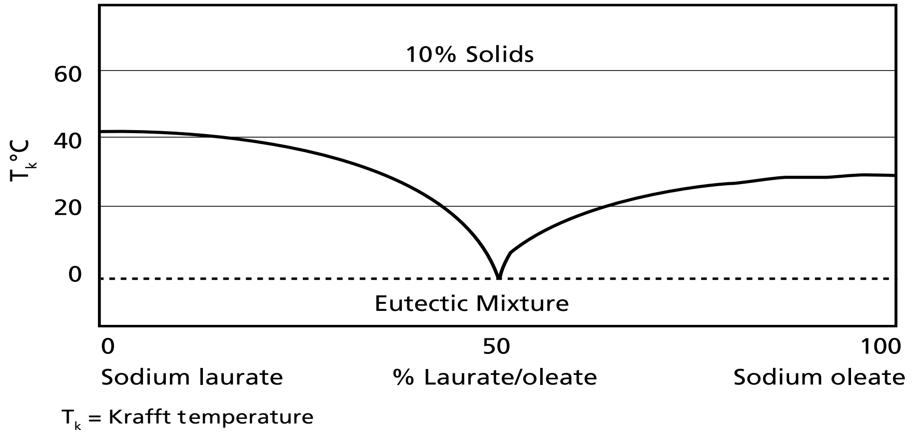


Figure 1.1 Solubility of the Eutectic Mixture from C12 and C18:1 Soaps.

A note on eutectics:

> *A* eutectic property *is a material property that exhibits very differently in a mixture than it does in any of the components of the mixture.*
>
> *Eutectic mixtures usually arise when the molecules of two (or more) of the materials have totally different shapes or sizes. Then the molecules of the mixture cannot pack together neatly. In the example mixture considered here, C12 saturated soaps have a straight chain of carbon molecules, whereas C18:1 unsaturated soaps usually have a U-shaped* (cis) *carbon chain. Each molecule "sabotages" the other so that the mixture cannot crystallize normally, and the abnormal crystals have higher solubility.*

In (almost) all soap tablets there will be more soap derived from C18:1 fatty acids than from C12 fatty acids; that is, most soap tablets contain more sodium oleate than sodium laurate. It therefore follows that as the C12 content is increased—as the soap contains more nut oil—so the amount of 1:1 oleate:laurate mixture will increase, and the lather from that eutectic mixture will increase.

There is also the potential for soap softness to increase with increasing nut oil level, but this is not observed. The explanation of why this could happen, but does not happen to any significant extent, is based on the first of two models, discussed next, relating soap structure and properties.

Soap Structure–Performance Models

Soap structure models are helpful because they provide ways to more easily visualize the links between formulation, processing characteristics, and user properties. There are two useful models of soap structure.

Model 1 is a very simple macro model based on solid soap to liquid soap phase ratios. This model is used to explain many aspects of processing characteristics.

Model 2 is a molecular model that considers the crystallization changes occurring during soap drying and subsequent processing, and it can be used to explain aspects of the user properties of soaps.

Model 1: The Macro Model

Soap bar hardness at constant moisture content and electrolyte content is a function of the balance between the following components:

- Solid (insoluble) soaps—mainly Na C16 and C18 saturated fatty acid soaps (sodium palmitate/stearate), but with some content of Na C12 saturated fatty acid soap (sodium laurate) when this has not had an opportunity to form the 1:1 eutectic mixture with Na C18:1 unsaturated fatty acid soaps (sodium oleate).
- Soluble soaps dissolved in the free-water content of the soap bar. These are mainly the very soluble 1:1 oleate:laurate eutectic soaps, plus some free Na C18:1 soap (sodium oleate), plus electrolytes, glycerine, and so on.

Simple macro model
Soap hardness at constant moisture content is a function of the balance between the solid insoluble soap and the softer soluble soap.

Solid/insoluble soaps	:	Softer/soluble soaps
Na C16/18 and any undissolved C12		C12/Ca18:1 eutectic + excess C18:1/18:2 in the water of the bar
Solid phase	:	Liquid crystal phase in the bar water

More solid/less liquid = harder
More liquid/less solid = softer

This simple macro model of soap structure and hardness can be very useful to explain many formulation and processing effects, and it will be referred to several times in what follows. This model simply shows a schematic balance between the solid soaps and the dissolved soaps. In real life, the "liquid phase" will be a solution of up to about 25% dissolved soaps, and such a high-concentration soap solution will have a solution liquid crystal structure. This means that although the soaps are dissolved, the soap molecules are arranged into large domains of micelles, and these have a regular packing structure. In most soaps, that structure will be a hexagonal close-packed arrangement of cylindrical or rod micelle domains.

Although it has a regular structure, the liquid phase remains mobile and fluid. Therefore, the more liquid phase there is in soap, relative to solid phase, the softer the soap will be.

Predictions of Effects from Formulation/Process Changes

Some of these effects will be intuitively obvious, but try to keep in mind how the model explains them.

Higher Temperature

At a higher temperature, more soap will dissolve from the solid phase into the liquid phase. The liquid phase volume will increase in size relative to the solid phase, and the soap should be softer.

Higher Water Content in the Soap

There are two effects of this change. First, the extra water will directly increase the liquid phase volume. Second, the liquid phase will (potentially) be able to dissolve more soap, giving a further increase in liquid phase volume. Both actions will lead to a softer soap, so a relatively small change in soap water content (say 1–2%) can have a big influence on product softness.

More Electrolyte in the Soap

By common ion and ionic strength effects, electrolytes (usually sodium salts of stronger acids) will salt-out soaps from solution in the liquid phase. The result will be less liquid phase volume and more solid phase, and a harder soap.

The hardening effect of electrolytes can be large. For example, an increase from 0.5% NaCl in soap to 1% NaCl will almost double the soap hardness from typically 2×10^5 N/m^2 to 3.8×10^5 N/m^2. The effect is large because all of that electrolyte will be dissolved in only the free water of the soap, which is typically 10% water. The overall 0.5% electrolyte is therefore present as a $0.5 \times 100/10 = 5\%$ solution, and the 1% electrolyte as a 10% solution. That is a big difference.

Always think of soluble soap component concentration effects in this way.

More Nut Oil in the Soap Oil Blend

Clearly, if a higher percentage of nut oil in a soap gives more lather because it allows the formation of more 1:1 oleate:laurate eutectic, then this same mechanism should mean that a higher nut oil content will give a softer soap.

If all else is equal, then this is true. However, all else is not normally equal. During manufacture, soap is washed with a strong solution of NaCl to remove the glycerine by-product. As the soap's nut oil content increases, a higher concentration of NaCl solution is needed to separate soap from the glycerine lye, and the residual soap will always contain more of the NaCl. This will increase the soap's hardness.

The softening effect of the eutectic and the hardening effect of the electrolyte just about balance out, and in practice, increasing nut oil content up to about 40% in a blend with 60% tallow or palm oil does not give a softer or harder soap. Above 40% nut oil, the tallow or palm oil no longer provides enough C18:1 to form more of the 1:1 eutectic. The additional C12 therefore stays as solid phase, and the soap will quickly get very hard as the nut oil content increases beyond 40%.

Free Fatty Acids

To improve their performance, some toilet soaps can be made to contain significant amounts, typically more than 5%, of free fatty acids (superfatting). Such free fatty acids can be part of the solid phase or solubilized in the liquid phase. In the liquid phase they will pack within the micelles, and, because they do not have a strongly polar head group, they will dilute the charge density at the micelle surfaces. The result is that the usual cylindrical or rod micelles can form a different, more stable structure—a lamellar structure. A lamellar liquid phase structure can inherently "hold" more dissolved soap and is much less viscous than a hexagonal liquid phase structure. The result is a larger liquid phase volume, and certainly a lower-viscosity liquid phase—and a softer soap.

Glycerine

Glycerine is very soluble in water, so it will always locate in the liquid phase. The first few percent of glycerine added to, or left in, soap will simply increase the size of the liquid phase (slightly) and will give a slightly softer soap. Glycerine levels of up to about 1% in a toilet soap, and perhaps 2% in a laundry soap, can have this effect.

At higher levels of glycerine, say 6%, such as would be present if you did not remove any of the residual glycerine from soapmaking, the effective concentration of glycerine in the liquid phase becomes very high. It can be close to 40% in toilet soap:

$$6\% \text{ glycerine in } 10\% \text{ free water} = (6/(10+6)) \times 100 = 37.5\%$$

Soap will not dissolve in strong solutions of glycerine, and if glycerine is added or increased to levels over about 2%, some dissolved soaps will be displaced from the liquid phase and become solid. In effect, a high level of glycerine acts like an increased level of electrolyte.

Minerals Added to Soaps

At moderate levels (say 5%, perhaps higher), any minerals will simply be dispersed evenly between both the solid and liquid phases and have little influence on soap hardness. At higher levels (say over 10%), minerals can disrupt the packing of the soap crystal domains which are the solid phase. Such disruption can lead to the domains being able to "slide over each other" more easily, giving the impression of a softer soap. However, the softness is due to weakness in the solid phase rather than to any change in the solid-to-liquid ratio.

Perfume

Perfume acts like free fatty acids—it quickly softens soap, probably because some of the polar ketone and aldehyde components quickly migrate into the liquid crystal phase. As more perfume components migrate into the liquid phase in the hours/days after soap manufacture, the liquid crystal phase can probably also change from the viscous hexagonal structure to the more fluid lamellar structure.

Model 2: The Molecular Model

This model considers the crystallization changes that occur during soap drying and subsequent processing, and it can be used to explain aspects of the user properties of soaps.

The mixture of oils from which soaps are made have a wide range of saturated and unsaturated fatty acid chain lengths, from below C8 to greater than C20. For the purposes of this model, only the three major chain length groups will be considered:

1. Sodium palmitate/stearate (NaP/St), C16/C18
2. Sodium oleate (NaOL), C18:1
3. Sodium laurate (NaL), C12

Soapmaking by normal alkali saponification, washing, and fitting produces a liquid neat soap phase with a 70% solution of soap at 100 °C minimum. This neat soap has no formal crystal structure, or at least no solid crystal structure. To make toilet soap noodles, the neat soap is preheated to typically 135–145 °C and is sprayed into a vacuum chamber, where it loses water to become 85% soap with around 12% water (and some residual electrolyte, glycerine, and so on). During the vacuum-spraying process, the soap cools and solidifies very, very quickly (in 0.5 sec) from, say, 140 °C to below 50 °C. This sort of very rapid cooling and solidification does not give enough time for optimum crystallization.

Instead, the soaps of all the different chain lengths crystallize into a metastable solid phase. Only some of the most soluble chain length soaps will remain in the residual water of the soap—sodium oleate (NaOL) and, in much lesser amounts, linoleate, and short-chain saturates such as C6 and C8.

Although it does not have the most stable arrangement/packing of the mixed-chain-length soaps, the solid phase produced at the drier does always have a well-defined way in which all the long carbon chains of the fatty acid parts of the molecules pack together. The details of this structural arrangement can be seen using X-ray diffraction techniques.

The structure of the solid phase formed immediately after drying is called the *kappa phase* (or the *omega phase* by some authors). Remember that the kappa phase will contain all the soap chain lengths:

Kappa phase = NaP/St, NaL, and even some NaOL.

Remember from the preceding that the best lather is obtained from Na laurate (NaL), but only when it is dissolved by forming the 1:1 eutectic mixture with NaOL. In the solid kappa phase resulting directly from the drying stage, almost all the NaL is "locked up," so soap directly from the drier has relatively poor lather.

The question is how to free the NaL from the solid phase so that it can form the eutectic mixture with the NaOL dissolved in the liquid phase. The answer is to provide "activation energy" in the form of mechanical work energy. Applied work will allow the metastable kappa phase to release some NaL into the liquid phase, where it will form the thermodynamically more stable eutectic with NaOL. As soon as some eutectic forms in the liquid phase, the liquid phase contains more soap and is a better oleophilic solvent, so it will more easily dissolve even more NaL from the solid phase. This process is self-perpetuating as long as the work energy continues to be applied.

All the NaL progresses could move out of the solid kappa phase into the liquid phase. As this movement of NaL progresses, it leaves "holes" in the kappa phase structure and makes it weak. As more and more NaL moves from the kappa phase to the liquid phase, eventually the kappa phase structure starts to collapse and then recrystallize.

Soap is not only mixed/milled and refined in order to evenly distribute perfumes, color and so forth, but also to change the crystal phase structure and to give soap with better user properties.

Implications of the Molecular Model

The nature of the phase to which the kappa phase will recrystallize depends on the type of soap. In particular, it depends on the solvent power of the liquid phase, that is, the water content and whether it contains any solubilized free fatty acids.

If the water content of a 90/10 to 70/30 type soap is at or above 15% (preferably 18%), then with enough supplied work energy, almost all of the sodium laurate will move from the solid kappa phase into the liquid phase. If enough NaL moves from the solid to the liquid phase to cause restructuring of the solid phase, then the solid phase will crystallize to what is called the *zeta phase* (or the *beta phase* by some authors).

Remember that the zeta phase will now contain only NaP/St soaps because all or most of the NaL has moved into the liquid phase. A characteristic of the zeta phase is that the crystal size is very small. This means there is less scattering (diffraction/reflection) of incident light, so soaps with high zeta phase content are often translucent.

Scattering is also minimized when the refractive index (RI) between two surfaces is at a minimum, here at the boundary between the solid phase and the liquid phase. Glycerine has a high RI (1.5), close to that of soap, and is very soluble in the water of the liquid phase. A high glycerine content will therefore increase the RI of the liquid phase to be closer to that of the solid phase, and will always enhance the optical effect of soap translucency.

It is relatively easy to get toilet soaps to form some zeta phase solid by applying mechanical work energy. A higher water content (at least 16%, rather than the usual 13%) will help the movement of NaL from the solid to liquid phases and, with enough work energy, can result in almost complete conversion from the kappa phase to the zeta phase.

High zeta phase soaps will always have better lather properties, because the liquid phase will contain a much higher proportion of the high-lathering NaOL:NaL eutectic mixture.

Formulation Limitations for the Molecular Model

Nut Oil Content

If a soap has less than 10% nut oil (equivalent to about 5% sodium laurate), then even when all the NaL moves from the solid phase to the liquid phase, this movement will not distort the kappa phase enough to cause any major recrystallization to the zeta phase.

If the soap contains more than 30–35% nut oil, then even when the liquid phase contains as much NaL as is possible, there will still be enough NaL remaining in the kappa phase to keep that phase stable.

Water Content

Most toilet soap has about 20% nut oil and about 13% water content, and only trace amounts of free fatty acids. Even if the maximum realistic amount of work energy is applied to such a soap formulation, only part of the NaL will move from the solid kappa phase into the liquid phase. There is simply not enough solvent power in 13% water to move enough of the NaL to cause the kappa phase to fully recrystallize to the zeta phase. Normal soaps therefore contain only a limited amount of zeta phase and are not translucent.

Fatty Acids

Soap with free fatty acid (FFA) content at more than 5% of the total fatty acid (TFA) content are often called *superfatted* soaps. The presence of such FFA can significantly modify the soap structure and user properties. Because the presence of FFA imposes significant processing constraints, superfatted soaps are less common today than they were in the period from 1970–1990. Most toilet soaps now contain zero or only fractional amounts of FFA.

If the soap being worked contains more than 5% free fatty acids, then both the solid phase and the liquid phase structures will change. The liquid phase structure will contain a lot of solubilized free fatty acids, and, as explained earlier, this will cause the liquid phase structure to become lamellar rather than hexagonal.

Under the influence of work energy (mixing or milling), the movement of NaL from the solid phase to the liquid phase is exactly the same as for nonsuperfatted soap, and so the kappa phase becomes more and more NaP/St only. However, when this structure collapses, it forms a phase with crystals much larger than those in the kappa phase (rather than much smaller, as is the case with the zeta phase). These larger crystals are long and ribbon-like and highly intertwined. This structure is called the *delta phase.*

Delta phase can only be formed in superfatted soap if all work energy is input at temperatures ideally below 38 °C, and certainly below 40 °C. If these ribbon-like delta phase crystals can be formed in the soap due to work energy input, then there can be significant advantages for the final soap performance. In particular, the mush can be reduced.

All soap mush is delta phase, whether it forms from a soap in which the solid phase is in kappa or zeta form, or is already in delta form. During soap mush formation, water penetrates into the soap bar. If the bar solid is kappa phase (NaP/St+NaL), then during the relatively long soap/water contact time needed to form mush, the NaL will dissolve out into the surrounding water, leaving the residual NaP/St to recrystallize into the delta phase in the presence of a lot of water. That water becomes trapped amongst the long, ribbon-like crystals of the delta phase and gives a highly mushing product. The net result is that kappa phase soaps inherently have high mush.

If the solid phase is zeta phase, then there is no NaL present to dissolve out into the surrounding water, but eventually, by Oswald ripening, the small zeta phase crystals will grow into the long, ribbon-like crystals of the delta phase, and will still trap the penetrated water. This growth probably takes a longer time to create the delta phase than does the NaL-loss-induced recrystallization by which it forms from the kappa phase. Therefore, all else being equal, a zeta phase soap should take longer to give the impression that it is a highly mushing product. But all is normally not equal. To encourage the initial formation of the zeta phase, a soap will normally have a higher water content, and, if it is to be a translucent soap, probably also a high glycerol content. Higher water or glycerol content both result in much greater water penetration, and this more than compensates for the slightly longer mushing time expected from the zeta-to-delta phase transformation.

The net result is that highly worked soaps can form mush more slowly, but usually other formulation characteristics that promote significantly increased mush are also present.

However, if the solid phase is already delta phase because the soap contained free fatty acids and was worked at temperatures below 38°C, then there will be less mush than from soaps with a kappa or zeta solid phase. The preformed delta phase does not trap the penetrated water in the same way that it traps water when the delta phase forms due to mushing.

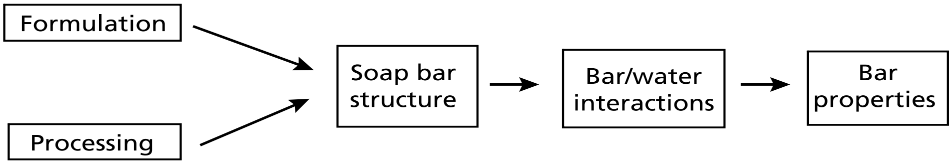
Soap/Water Interactions

So far emphasis has been on how formulation and processing influences soap structure. Now it is appropriate to consider how soap structure influences bar/water interactions, and how these in turn affect bar properties.

There are numerous examples of how aspects of the formulation of a soap bar influence its user performance properties. For example, higher water content usually gives a softer soap that will absorb more water and generate more mush as it stands, wet, on the wash basin. That same soap then usually shows more cracking during use. Similarly, a soap bar formulated with a high percentage of nut oil in the oil blend will, through formation of more of the oleate:laurate eutectic mixture, generally lather more easily and create more lather during use. Whether that extra lather is appreciated or desired is another issue that depends on wash habits and the hardness and temperature of the available water.

Earlier sections have shown how the processing of the soap bar influences its user properties. For example, again considering soap with higher water content, supplying a significant amount of extra work energy (through intensive mixing or milling) will make the product very hard and impart significant translucency, by causing a kappa-to-zeta phase change.

A general relationship can be shown as follows:



That is, there is a direct link between formulation/processing and soap properties, with soap structure and bar/water interactions as intermediate steps. A key element of these relationships is how soap/water interactions influence the bar's user properties.

Mush and Cracking

Soap mush and cracking are two of the most visible negative properties that can result from soap/water interaction. Soap mush and cracking effects are related. The relationships between the two effects can be seen by making some assumptions about soap cracking:

- The fundamental cause of cracking is stress applied to inherent weaknesses in the structure of plodded soap bars.
- This weakness in the structure arises when processing makes solid soap crystals align in specific ways.
- The types of soap crystals formed in a soap bar can be influenced by the formulation.
- The stress on the soap structure that leads to cracking occurs when soap swells due to water uptake by the liquid phase during mushing, and shrinks when the mush dries.
- The amount of mush, and therefore the resultant stress, are influenced by both formulation and processing.

These propositions imply that to understand the causes of cracking requires an understanding of the following:

- How soap structure is influenced by processing and formulation
- How water interacts with soap to form mush.

The Source of Structure Weakness

The Fundamentals of Structure

Rapid cooling of soap in a drier gives a product with most of the sodium laurate, and even some sodium oleate, locked into a relatively insoluble solid kappa phase, along with sodium palmitate and sodium stearate. Work energy during subsequent processing will provide the activation energy needed to cause most of the laurate soap (C12) and some of the oleate soap (C18:1) trapped in the solid kappa phase to move into the liquid phase. In the liquid phase, which already contains some of the more soluble sodium oleate, the oleate and laurate will form a 1:1 eutectic solution with greatly increased solubility. The increased solubility and amount of soap present will be sufficient to allow the soluble soaps in the free water to form into micelles. The micelles will pack into either hexagonal close-packed or lamellar liquid crystal structures.

Soap is therefore a mixture of two components:

1. Asymmetric solid-phase crystals, predominantly of insoluble sodium palmitate and sodium stearate, but probably including some residual sodium laurate. These crystallize into relatively large asymmetric crystals or domains of crystals.
2. A liquid phase consisting of water containing soluble soaps, electrolyte, glycerol, free fatty acids, perfume, and so on.

In most soap tablets, the liquid phase will mainly be a liquid crystal, rather than an isotropic solution. The liquid crystal forms when the solution contains enough soap to form large micelles composed of very soluble soaps, such as the oleate:laurate eutectic mixture, and of very soluble, very short-chain-length soaps, such as C6 to C10 types. The liquid crystal phase may also contain free fatty acids, perfume, and other compounds, solubilized in the micelles.

Most 80/20 non-nut oil/nut oil type soap tablets will contain about 80 parts solid phase and 20 parts overall liquid phase, with a hexagonally structured liquid phase that occupies twice the free water content. The liquid phase of soap containing high levels of free fatty acids can have lamellar structure and occupy about three times the free water content.

Pressure Effects during Plodding

Neither the solid phase nor the liquid phase is continuous throughout a final soap bar, but individual, microscopic areas of the bar (domains) may have a continuous solid or liquid phase. Importantly, if you “squeeze” soap hard enough, some of the liquid phase will separate from the solid phase. The pressures experienced during soap plodding are typically 60 kg/cm^2 and are high enough to give some separation of this type. This is especially true if the liquid phase contains some low-viscosity isotropic solution as well as the usual high-viscosity hexagonal liquid crystal phase. The liquid phase that separates will normally also contain some glycerol and electrolyte residual from soapmaking.

The separating liquid phase has two effects:

1. It coats the solid-phase crystals, making it much more difficult for the plodder to make them coalesce into a homogeneous bar. Thus, too high a plodding pressure can increase soap cracking.
2. Solid soap crystals, are relatively hydrophobic, and water will not penetrate through them. Therefore, when soap is immersed in water, the water will first enter the soap via any physical channels between crystals. These physical channels are regions between coalesced soap noodles. If these regions contain liquid phase material that has been squeezed away from the solid phase during plodding, then the liquid phase will swell, because it absorbs water to try to dissolve. The swelling will further reduce cohesion between the soap noodles.

A corollary is that if you add water to soap noodles/pellets after drying, then it may dissolve only a small amount of soluble soap and remain as an isotropic solution mixed with the solid phase and the liquid crystal phase. This isotropic solution has low viscosity relative to the much more concentrated and structured liquid crystal phase, and therefore is more likely to be squeezed out by plodder pressure and is more likely to increase cracking. Thus, adding water at the mixer can increase cracking.

Crystal Orientation during Plodding

Recall that if you float sticks of wood in a river, the sticks will turn to have their long axes parallel to the direction of the water flow. The domains of solid-phase crystals in a soap bar are asymmetric, like the sticks, and as the soap mass moves during plodding, many of the asymmetric soap crystals will similarly align themselves parallel to the direction of soap movement.

Maximum alignment occurs when there is shear applied to the moving soap mass. In particular, this will occur when part of the moving soap mass is next to a relatively stationary surface, for example:

- A part of the plodder, such as the barrel wall
- The surface of the plodder screw, which often moves at a different rate from the soap mass
- Other areas of the soap mass that are not moving at the same time or at the same rate.

During extrusion with a screw-action plodder, there are many opportunities to generate such shear and to cause large-scale crystal alignment.

Consider the first example in the previous list, shear between the soap mass and the plodder barrel. Although there already may be some alignment of crystals in the pellets that are fed to the plodder (because of shear during screw extrusion from the drier), this will largely be offset by the random mixing of pellets as they feed into the plodder. Once the pellets are compressed, they will shear against the barrel wall and also against the screw surface.

This shear will introduce an order to the crystals in the soap mass such that, at the point of entering the plodder cone area from the screw, the soap crystals are typically perpendicular to the main longitudinal axis of the plodder. The appendix at the end of this chapter shows details of why this is so.

Now remember that at any point in time soap flows into the cone from only a small section at the very end of the plodder screw. Soap does not flow uniformly from the screw across the whole input face to the cone. Once the cone of a plodder has become packed with soap, most of the soap will be moving forward at a much slower rate than that entering the cone (under pressure) from that small section at the end of the screw. Therefore, in the cone there will be significant shear between faster-moving and slower-moving areas of soap. That shear causes reorientation of the soap crystals. The crystals that entered the cone oriented perpendicular to the longitudinal axis of the plodder (and therefore perpendicular to the soap flow) will reorient themselves to become parallel to the longitudinal axis of the plodder and to the soap flow. This reorientation is likely responsible for much of what is often called "work softening" of soap in a plodder, and it significantly influences the direction and extent of subsequent water penetration and cracking during product use.

It is sometimes easier to visualize this reorientation and subsequent flow in the plodder cone by considering a plodder fitted with a multihole pressure plate between the screw and the cone areas. Generally such a pressure plate is not recommended because it will cause a temperature increase. However, imagining this configuration sometimes makes it easier to visualize how some candles of soap entering the cone will move faster than others and how the shear between them will encourage crystal orientation to be parallel to the direction of soap flow.

The rods or candles of soap formed by a pressure plate will deform as they travel through the cone. They will retain their individual candle structure, but they will become thinner. They become thinner because soap accelerates as it moves through the cone. Soap entering a 300 mm diameter cone at 1 cm/s (2.5 tons/h) must leave at 25 cm/s through a typically 60 mm final orifice plate aperture. As circular candles of plastic soap are forced together by pressure in the cone, they adopt a hexagonal packing.

When the soap flow in the cone reaches the orifice plate, there will be some distortion of the soap crystal patterns as soap builds up behind the plate. Then, as the soap flows around the edges of the orifice, there will be more shear and another reorientation of soap crystals such that the compressed candles of soap in the extruded bar will again have crystals oriented parallel to the direction of soap flow.

Visualizing Soap Structures in the Plodder

An alcohol immersion procedure allows visualization of crystal orientation during soap flow through a plodder cone in the extruded bar, cut slug, and final stamped tablet.

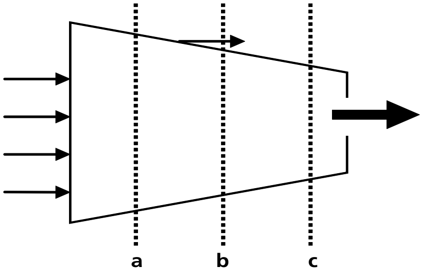
The steps of the procedure are as follows:

1. Cut a smooth surface on the soap section (ideally with a microtome or carpenter's plane).
2. Immerse the cut surface in deionized water at 20 °C for an hour. Water penetrates into the soap via the liquid phase surrounding any solid phase crystals and causes the liquid phase to swell.
3. The wet soap surface is then soaked in a solution of at least 95% alcohol for an hour, during which the penetrating water and associated liquid phase is rapidly removed from the soap.
4. Finally, the soap surface is allowed to dry naturally at ambient temperature.

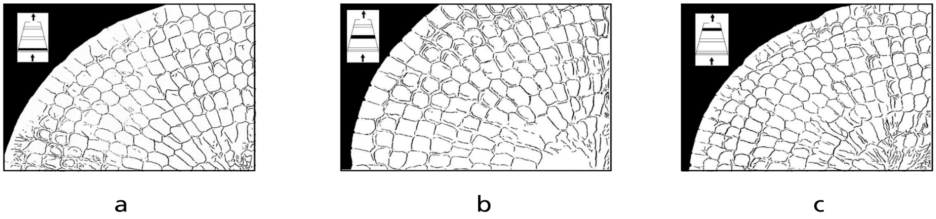
Typically, after about 1 hour of drying, it is possible to see a pattern that corresponds to the areas of solid phase and liquid phase in the original soap.

The alcohol immersion procedure can be applied to the surfaces of sections of soap cut from the soap block removed from a plodder cone. This shows that the individual candle structure is retained through the entire cone.

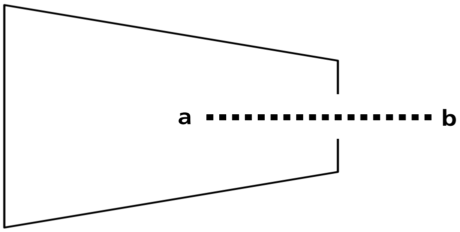
If you take slices cut from the plodder cone at the points a, b, and c, and then perform the alcohol immersion procedure on one side of each slice, the pattern of the original candles is seen to survive more or less unchanged through the cone. All that happens is that the candles become slightly smaller in diameter and more hexagonal in profile as they come closer to the orifice plate and the cone pressure increases.

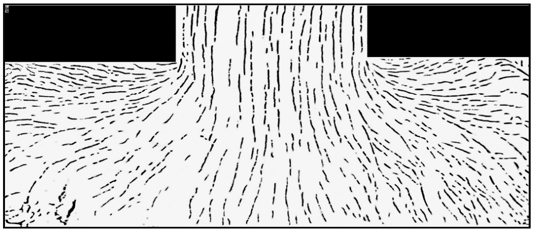


If you take a block of soap from just behind the orifice plate of a plodder cone, and cut it in another direction, parallel to the direction of extrusion, then the alcohol immersion procedure shows a representation of the general orientation of solid-phase crystal domains parallel to the direction of soap flow, and a much more pronounced orientation in the same direction being introduced as the soap encounters significant shear at the orifice plate.



A section through a…b will show the flow line pattern made by orientation of the solid-phase crystal domains.





The greater parallel orientation in the final slug is quite obvious, as is the orienting effect of shear at the corner of the orifice plate.

The Overall Effects

In the cone and in the bar or slug that emerges from the orifice plate, there are compressed candles of soap with surfaces made of soap crystals oriented with the long axis parallel to the direction of extrusion. Surfaces with such parallel crystal orientation do not easily adhere together.

Consider an analogy with the mineral talc. Talc is smooth and slippery because the talc crystals are flat plates, and these become oriented in the same direction as the bulk mineral experiences shear when rubbed between layers of skin.

Because of pressure effects in the cone, these candles may have surfaces coated with relatively low-viscosity liquid-phase material containing soaps, electrolyte, and glycerol. This will significantly reduce the adhesion between soap candles. Indeed, an electrolyte and glycerol solution is sometimes used as a lubricant to stop soap from sticking to soap dies during stamping. Therefore, plodded soaps inherently have planes of structural weakness. The lines of weakness are parallel to the direction of extrusion, and they will form whether or not you use a plodder pressure plate.

Another simple way to see these lines of weakness is to take a freshly plodded length of soap, grip each end, and “twist” the bar along its length with alternate clockwise and counterclockwise hand movements. The weaknesses in the structure will cause the bar to delaminate quite quickly into the remnants of the original candles.

Consequences of Structural Weakness

Soap does not crack until it is used in water and allowed to dry (unless you have done something very, very wrong in the formulation or process). It is not the water that makes soap crack; it is the behavior of mush as it is formed when water penetrates into the soap bar, and especially as it dries. Therefore, to understand cracking we must understand mush.

What Is Mush?

Mush is the soft, paste-like layer that forms on soap when it is in contact with water. Typically it forms when soap is left on the side of the wash basin after use.

Mush consists of very long, twisted, insoluble soap crystals intermixed with a liquid, which may be an isotropic solution or in the liquid crystal phase, or both. Very close to the soap surface the liquid has a high soap content and is a liquid crystal, whereas further from the surface it is an isotropic solution because there is not enough dissolved soap to have a defined structure. From the soap surface to the true solution, mush therefore has a variable composition and a somewhat variable structure, and it is dynamic—the water penetrates and the soap dissolves during all the time that they are in contact.

The Solid Phase of Mush

Most of the insoluble solid phase of mush is sodium palmitate and sodium stearate (C16 and C18 soaps). These soaps have the long, twisted crystal form (delta phase) because during the long water contact time of mushing, any residual, more soluble soaps (sodium laurate or even sodium oleate) in the bar's solid kappa phase will dissolve. The solid phase in most soap bars, for example, the common 80/20 type, will be either:

- Kappa phase (relatively large crystals containing all the soap chain lengths). This sort of solid phase is found only if soap has not been worked very hard by mixing, milling, and other processing steps.
- A mixture of kappa phase and zeta phase. This phase mixture is found in most soaps. The zeta phase component consists of very small crystals of sodium palmitate and stearate formed by recrystallization of the kappa phase when work energy input encouraged the more soluble sodium laurate to move to the liquid phase.

During prolonged contact with water:

- Any kappa phase solid will lose laurate to the water, the phase structure will weaken, and the kappa phase will recrystallize to the large crystals of the delta phase.
- Any zeta phase crystals may grow (via Oswald ripening), because this will decrease the area of the boundary between the solid and liquid phases: a few big crystals have a smaller surface area than many small crystals. As they grow, the structure becomes better considered to be in the delta phase rather than the zeta phase.

Remember, zeta phase and delta phase are chemically the same: primarily sodium stearate and sodium palmitate soaps. They differ only in molecular arrangement and crystal size.

To summarize, the solid phase of mush is large crystals of delta phase, and because the crystals are large they are always opaque, even when they come from energetically worked translucent soaps.

The Liquid Phase of Mush

Water penetrates into a bar of soap via the liquid phase. The liquid phase absorbs water by osmotic pressure, which tries to dilute the liquid phase. This causes the phase volume to increase and is observed as swelling of the wetted soap surface.

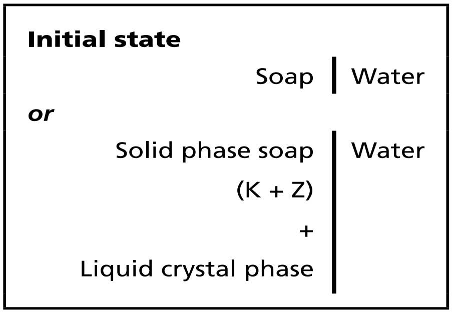
There are now two effects:

1. The water penetrating the soap dilutes the liquid phase. In the limit, it can dilute the liquid phase enough that an existing liquid crystal component no longer has a high enough concentration to remain as a liquid crystal, and it reverts to a simple isotropic solution.
2. During the long soap/water contact time of mushing, some sodium laurate and sodium oleate will dissolve from the solid phase into the water. These dissolving species can now increase the concentration of dissolved soap and make it more likely that the liquid phase is a liquid crystal.

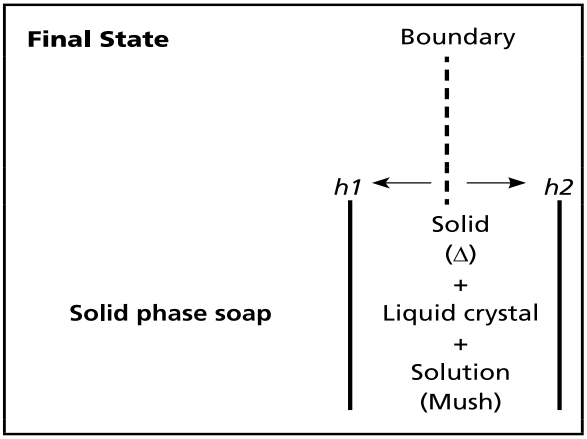
Which effect predominates depends on where you are in the mush layer.

Clearly, it is most likely near the soap surface that the penetrating water will contain a lot of dispersed solid phase and have a liquid crystal character. Farther away from the surface, the liquid will have less structure and it will contain less dispersed solid phase, until eventually it becomes an isotropic solution only, with no solid phase.

A pictorial model of the mushing process can be given as follows:



Initially there is a sharp boundary that separates the bar's solid and liquid crystal phases from the water with which the bar is in contact.



After a period of time, water will have penetrated into the bar to a depth of *h1*. The water cannot penetrate via the solid soap phases. The water penetrates via the liquid crystal phase, so that the liquid phase now contains more water and has a bigger phase volume, that is, it will swell. The swelling action then pushes the soap-to-solution boundary forward to point *h2*. Some of the soap will have diffused completely out of the soap into the water to form true solution, so the outward movement to *h2* is not as great as is theoretically possible.

The total thickness h of the mush layer is the sum of water penetration + liquid phase swelling, that is, $h = h1 + h2$.

A number of processes contribute to bar/water interactions such as water uptake by diffusion through the liquid phase. This can be impeded by solid phase crystals that are co-mixed with the liquid phase, adding to the tortuosity of the diffusion route.

Swelling of the Liquid Crystalline Phase

This depends on the structure of the liquid crystal phase (hexagonal or lamellar) and will be less if the soap in the liquid crystal phase is more soluble, in particular if work energy applied to the soap has enabled formation of more of the 1:1 oleate:laurate eutectic mixture.

Dissolution of the Liquid Crystalline Phase

This also depends on the solubility of the soaps in the liquid crystal.

The water absorption and swelling of the liquid phase will eventually continue until all the soluble soap has dissolved and diffused away from the bar surface into true solution. However, that process is hindered by the presence of the solid soap phase, which in general is in the form of large, ribbon-like delta phase crystals that can significantly impede diffusion.

Recrystallization of the Solid Phase

This can change the morphology of the solid phase and therefore the structure of the mush layer, or it may release soluble soaps, which then move into the liquid phase to further influence dissolution and swelling of that phase.

Mush is Delta Phase

That is, mush from any soap is *always* the long, ribbon-like crystals of sodium palmitate and sodium stearate. If delta phase is formed because of mushing, that is, by water penetration, then close to the bar surface the delta phase structure traps much of the penetrated water. The result is perceived to be a soap bar with high mush.

If the soap bar contains preformed delta phase before contact with water, then that implies that work energy has already persuaded a lot of the laurate trapped in the kappa phase at the drier to migrate into the liquid phase. In normal 80/20 soaps, this work-energy-induced migration causes the kappa phase to recrystallize to the small-crystal zeta phase. When the bar is subsequently in contact with water for a long time, the zeta phase *slowly* changes to delta phase through Oswald ripening. However, for some types of soaps (superfatted soaps = higher nut oil soaps with >5% free fatty acids) the recrystallization induced by work energy input is from the kappa phase to the delta phase, rather than to the zeta phase. Made under the correct process conditions (high shear at temperature <37 °C), these soaps have a low perceived mush because the delta phase is preformed in the bar and no longer traps the penetrating water during mushing.

Stress

When a soap forms mush, it also swells because of the water uptake into the liquid phase. However, that water uptake alone is not enough to deform the soap structure and cause cracking. Cracking occurs when the mush dries. When a mushed soap dries, the swollen soap shrinks again. A contracting soap film adhering to a surface will put stress on that surface. When the stress is across a plane of weakness in the soap structure formed by the alignment of crystals in the soap mass during plodding, the result is cracking.

Initially the crack may not be big enough to be visible—call that a “micro-crack.” However, the next time the soap is wet:

- Water will penetrate more deeply into that micro-crack.
- The mush formed in the micro-crack will take longer to dry out than mush on the normal surface of the bar.
- There will be an extra stress when the mush does dry out.

The micro-crack eventually becomes a visible crack.

The Fundamentals of Water Penetration

Osmotic pressure difference is the fundamental cause for water penetration into soap. Obviously, water does not penetrate into soap via the solid phase crystal domains. These are solid and hydrophobic.

Water penetrates via the liquid phase. The liquid phase is a relatively concentrated solution of electrolyte, of glycerol, and especially of soluble soaps. The driving force for water to penetrate will remain so long as there is a concentration difference between the liquid phase and the surrounding water.

In theory, there will always be a concentration difference, because the surrounding water can be regarded as infinite in extent and containing no dissolved material. In practice, soaps normally form mush when they are left in contact with a relatively small amount of water in a soap dish or on the side of a wash basin. Eventually this surrounding water contains so much dissolved electrolyte, soap, and so on, that the rate of further water penetration is very low. In effect, all of that small amount of water has become part of the mush.

Formulation and Water Penetration

The types of soaps in the liquid phase will influence the water penetration. If the soaps are very soluble—for example, are present as the oleate:laurate eutectic mixture plus very-short-chain types such as C6, C8 soaps—then much less water needs to be absorbed into the liquid phase to get those soaps into a low-viscosity isotropic phase where they can diffuse away from the bar.

Conversely, if the liquid phase contains relatively low levels of oleate:laurate but significantly more of the much-less-soluble free oleate, then much more water will need to be absorbed to form an isotropic solution.

No matter how much soap is present in mush, consumers perceive mush with more water as “high mush” and mush with less water as “low mush.” However, that is not relevant to a story about cracking.

What is relevant is that in both high and low mush cases, the mush contains the same amount of soap, just different amounts of water. Remember that the only mush seen by the consumer is mush on the soap bar, which is made up of both soap and water. Another way to think about this is that low mush soaps have more soluble mush that “disappears” into solution, so it is not seen as mush.

Note: The previous statement applies strictly to mush determined by the immersion test. In that test, the soap, cut to a defined size, is in contact with a nominally "infinite" volume of water, so that there is always a concentration gradient and water always penetrates into the soap bar. The same statement will hold for soaps in contact with a limited amount of water, but the numerical data may be quite different.

Other major elements of the formulation also influence water penetration:

- Glycerol—At the levels normally found in soap, glycerol generally increases the osmotic driver for water penetration and therefore increases mush. However, note that at high levels of glycerol (>5%) there is an opposing effect: glycerol limits the solubility of soap in the liquid phase, effectively decreasing the overall phase volume. Apart from also giving a harder soap, the lower phase volume decreases the water penetration.
- Electrolyte—This has a very similar effect to glycerol, but at much lower levels, for example 0.5%, rather than 5%.

Remember that these solubility-limiting effects from glycerol and electrolyte are in addition to those from the effects of pressure in the plodder cone "squeezing" liquid phase from the soap and causing it to inhibit adhesion at the candle interfaces. The net effect is still the same: more glycerol or electrolyte in the liquid phase means poorer candle adhesion.

Interesting Effects of Mush

The following effects have no practical importance and are included here only because they can help understand soap structure.

Annealing

If you heat a bar of soap for 16 hours at 75 °C, sealed so that there is no water loss (annealing), then the mush will halve as measured by the immersion test. A typical 80/20 soap will have mush reduced from 7.5 g/50 cm^2 of originally immersed surface area to about 3 g/50 cm^2. That is a very significant change, and one that would easily be noticed by the consumer. Although I have no record of it ever having been examined, I believe the soap cracking will also decrease significantly.

A mass balance experiment shows that the reduced mush of annealed soap is due to much less water being present in the mush removed from the soap. The soap contents of the mush from soap are the same with and without annealing.

The hypothesis is that during the high-temperature annealing process, some of the normally insoluble soaps (sodium palmitate and sodium stearate) also dissolve in the liquid phase, but then crystallize out again when the soap is cooled. However, no shear or stress is applied to the soap during the relatively long time of natural cooling, and this gives a very compact and well-ordered soap structure. It is much more difficult for water to penetrate into such a compact structure—there are fewer channels of structural weakness for water penetration (equivalent to a significant increase in tortuosity), less mush formation, and less crack-producing stress when the mush dries.

Mush and Bar Moisture Content

Water penetration and mush formation increase with the water content of the soap at the time of processing (mixing, milling, and especially plodding). Post-processing water loss will not markedly change the subsequent water penetration and mush. It is as if the soap has a "memory" of the water content at which it was originally made!

This effect occurs because during natural drying of a soap bar, some soluble components from the liquid phase will mainly precipitate as solid-phase oleate:laurate eutectic mixture (sometimes called *eta* phase), but as very, very small crystals dispersed as an intimate mixture with the liquid phase.

When this intimate mixture is rehydrated during water penetration and mush formation, the small crystals will dissolve very rapidly—so rapidly that the rehydration step will not influence the rate of water penetration.

The Implications of Structure and Mush for Cracking

Control the Formulation

We should control, to the extent possible, the formation of soap structure weaknesses that run parallel to the direction of extrusion. This is not easy because the formation of such weaknesses is inherent in the way extruded soap is made. However, the following can reduce weaknesses:

- A formulation low in electrolyte and glycerol to improve candle adhesion
- A formulation with appropriate plasticity

Unfortunately, nobody has ever been able to define or quantify what is an "appropriate" amount of plasticity, other than to say it is an amount that gives minimum cracking with a given equipment configuration.

Processing to Give Phase Optimization Can Help to Minimize Cracking

There are two phase optimization goals:

1. Maximizing the recrystallization from kappa to zeta phase in normal soaps (those without significant levels of free fatty acids). This also means moving laurate from the kappa phase into the liquid phase, thus giving a liquid phase with more of the oleate:laurate eutectic mixture and hence less water penetration, less liquid phase swelling, and less mush.
2. Generally, this means processing normal soaps at 45–47 °C to improve solubility of laurate in the liquid phase. It may be necessary to adjust the oil blend to allow such temperatures to be used and to also get a good bar finish and line efficiency.

Similarly, maximizing the recrystallization from kappa to delta phase in soaps with significant levels of free fatty acids will also give a liquid phase with more oleate:laurate, less water penetration, and less mush.

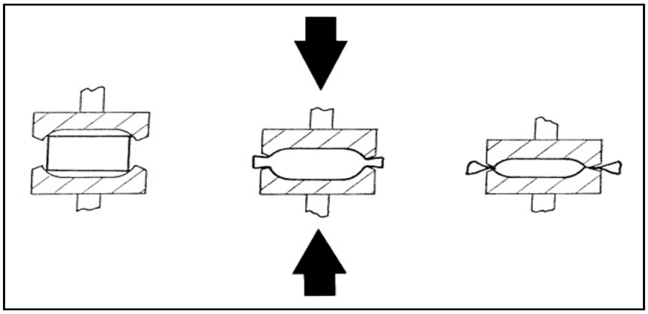
However, this type of soap containing significant amounts of free fatty acids must be processed at 35–37 °C, and certainly below 40 °C. At any higher temperature, the free fatty acids solubilized in the liquid phase act as an excellent lipophilic solvent and will also dissolve some sodium palmitate and sodium stearate from the solid phase. When such soap is subsequently cooled, the sodium laurate from the liquid phase co-crystallizes with the sodium palmitate and sodium stearate to reform the kappa phase. This leaves the liquid phase containing an even greater excess of sodium oleate as soap. Sodium oleate is much less soluble than the oleate:laurate eutectic, and much more water must be absorbed before it will dissolve. This means more swelling with water penetration, more mush, and more stress on the soap when it dries, that is, potentially more cracking.

It is very difficult to process soap at below 37 °C through all of the working stages of a finishing line.

Processing Can Help with Soap Flow and Orientation Effects

Soap Flow

A shaped bar (tablet) of soap is normally formed from a rectangular block or slug produced from the plodder by compressing it, quickly, between two shaped surfaces (stamping dies).



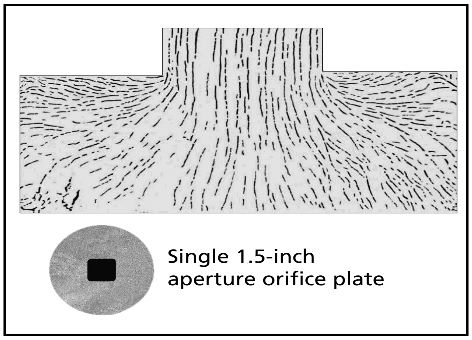
The soap flows as it changes shape in the die. Pressure and soap flow in the die can help remove some of the structural weaknesses introduced by the plodder, but unless both the slug shape and the final bar shape are properly designed, they can introduce new potential weaknesses, which may lead to cracking. In the simplest case, and especially for bandless bars, this means maximizing the flow of soap in the die, so a square or round slug is best to produce a generally rectangular bar.

Often it is noted that cracking occurs more frequently on one side of a finished tablet face than on the other. The following sections explain how such an effect can occur and how to minimize the problem.

Orientation Effects at Extrusion

Soap cracking generally, and especially cracking that is predominant on one soap face, can be significantly reduced by appropriately selecting the extrusion orifice plate and the orientation of the cut soap slug at the stamper.

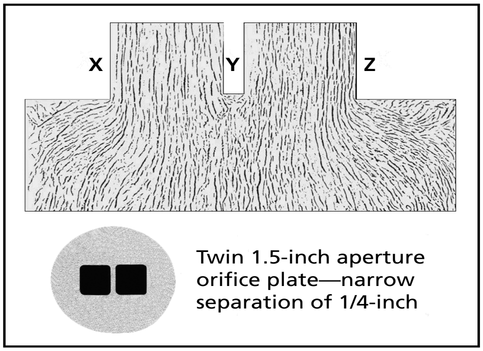
Earlier it was described how structure lines are produced in a slug as it is extruded through a single, rectangular orifice plate (die plate/eye plate).



Single 1.5-inch aperture orifice plate

The pattern of flow lines (lines of potential structural weakness visualized using the alcohol immersion procedure) are reasonably even on both sides of the slug.

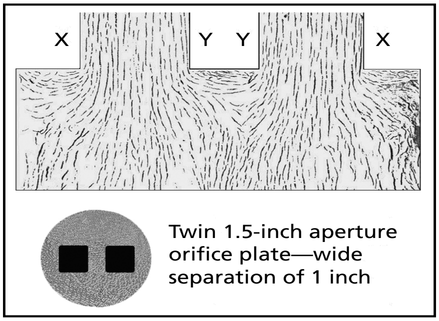
Now consider the situation where two slugs are produced side-by-side and close together from twin rectangular apertures in the same orifice plate. This is a common manufacturing method.



Twin 1.5-inch aperture orifice plate—narrow separation of 1/4-inch

The pattern of flow lines is now uneven. There are more flow lines and more regular flow lines on the outside faces of the slug (X) than on the inside faces (Y). This implies some significant structure difference between the outside and the inside slug faces.

Next consider the situation where the rectangular apertures in the orifice plate are much further apart, ideally a minimum of 45 mm at commercial scale.

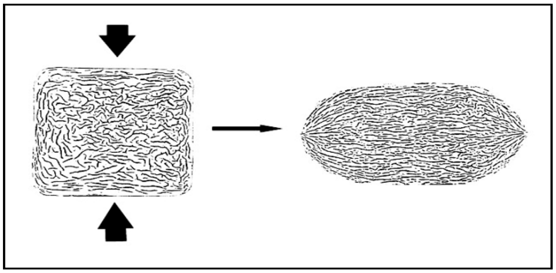


Twin 1.5-inch aperture orifice plate—wide separation of 1 inch

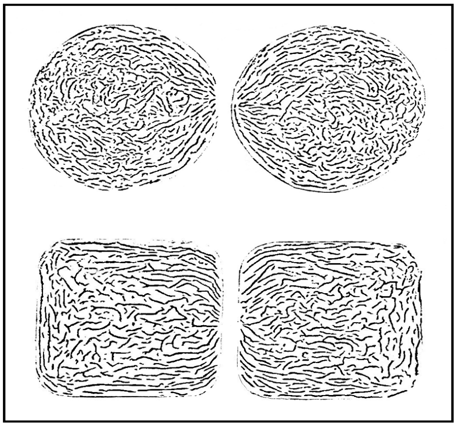
The pattern of flow lines is more even on both the inside faces (Y) and the outside faces (X) of each slug. Although the patterns at X and Y are not exactly the same, separating the apertures on the orifice plate has made each slug have a structure much more like that of a slug produced from a single aperture.

The implications for soap cracking of uneven flow lines on the inner and outer faces of a slug are best explained by again using the alcohol immersion procedure to show the flow line patterns in cross section through slugs and stamped bars, perpendicular to the direction of extrusion.

A square slug from a single-aperture orifice plate has a uniform pattern of stress lines. When stamped across any opposing faces, it will give a bar with a uniform pattern of stress lines, in which the outer flow lines follow the profiles of the slug edge and, in particular, the tablet edge.



Remember that the slugs produced through two apertures that are close together had more flow line orientation on the outside faces of the slugs than on the inside faces. This shows well in the cross-sectional pictures from rectangular or round slugs.



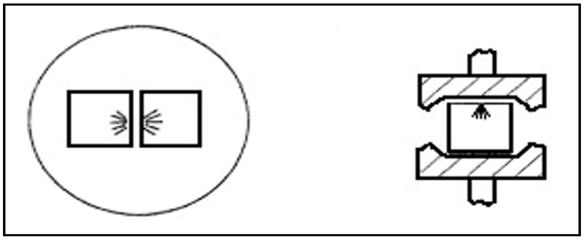
Note that between the slugs, where the previous view (horizontally through the cone end and slug) showed fewer and more irregular flow lines, there is now a clear indication that the flow lines are significantly perpendicular to the slug surface rather than parallel.

The effect is very similar to what will occur if a larger slug is simply cut vertically at the center, which is, in effect, what the narrow separating bar in the orifice plate has done.

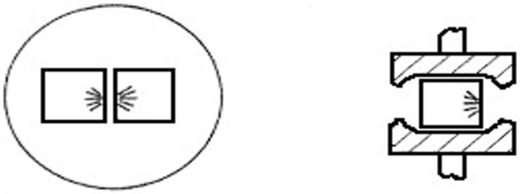
Orientation Effects during Stamping

There are now two ways in which such an asymmetric slug can be stamped.

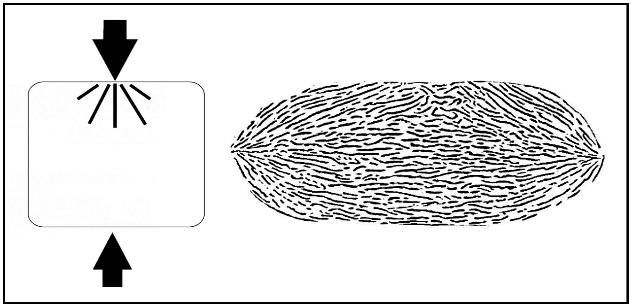
Inner face of the slug on the bar face:



Inner face of the slug on the bar edge:



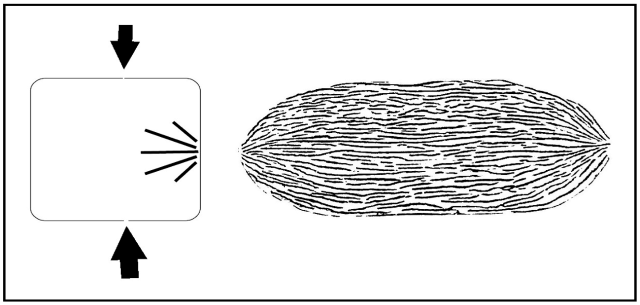
View these together with the final bar structures:



Clearly, when the final face of the tablet originates from the inside face of the slug, it also retains the poorer structure of the slug. The poorer tablet structure allows easier water penetration, more mush, and eventually more cracking. Importantly, the cracking will predominate on one face of the tablet.

Typically, 15% of such bars will crack in a home use placement test. The majority of the cracking will be on just one face of the bar.

When the soap slug is stamped with the inner face presented to what will eventually be the peripheral edge of the tablet, the flow line pattern is much more even at the tablet faces, and the irregularities from the inner face of the slug are largely removed with the soap flash from the stamping die.



Typically only 4% of such bars will crack in a home use placement test. Any face cracking is likely to be equal on both bar faces. End or "flash line" cracking may increase slightly, but consumers are not so deterred by such cracking.

The best practical solutions are the following:

- Ideally, only extrude soap using a single-aperture orifice plate with a nearly square aperture.
- If double-aperture orifice plates must be used, then use maximum separation between the apertures. At least 45 mm is recommended.
- If double-aperture orifice plates must be used, then make sure that when the slugs are stamped, they are oriented so that the inside faces of the slugs are on the bar edges.

Effects of Formulation on Cracking

General Notes

The precursors to cracking are:

- Water penetration
- Mush formation and swelling
- Mush drying and shrinkage

These factors will lead to stress on any structure with inherent weaknesses, for example, from crystal alignment. Any factor that influences these precursors will therefore also influence cracking.

Special Note on Materials Added at the Mixer

If the soap structure is not homogeneous because it is not well mixed, then this will lead to different rates of water penetration into different parts of the bar, and to correspondingly different levels of mush, mush drying, shrinkage, and stress. Such differential effects will certainly lead to increased cracking.

In particular, a soap may be inhomogeneous because the process route seeks to mix relatively high levels of soluble or fatty components after the basic soap noodle has been dried. In the simplest case, it is never advised to add more than 1% of water to soap noodles in a ribbon mixer; also, it is easy to observe that adding high levels of perfume (>1.5%) or fatty acids will make soap noodles very slippery and difficult to mix into a properly homogeneous mass. Homogeneous mixing is possible, but is difficult and time consuming.

Very high levels of hydrophilic additions can dilute the liquid crystal phase so much that it will revert to a isotropic solution with very low viscosity, which is much more likely to be forced onto the surfaces of candles in the plodder, giving rise to increased cracking.

Temperature Effects

Temperature is a physical condition, rather than a formulation characteristic, whose main effect is to modify the relative compositions ("formulations") of the solid and liquid phases.

Generally, for most soaps, increased temperature during processing gives lower cracking. The exception is any soap for which increasing the temperature also increases mush. This is the case for superfatted soaps containing more than 5% free fatty acids.

Higher temperature gives less cracking because at higher temperatures more laurate dissolves from the solid phase into the liquid phase, where it forms very soluble oleate:laurate. This leads to a significant increase in the liquid phase volume. More liquid phase and less solid phase in turn means a softer, more plastic soap. The softer, more plastic soap candles adhere better during plodding without the use of excessive pressures that could force liquid phase onto the candle surfaces.

In addition, if the liquid phase is rich in oleate:laurate, then it will contain more ordered, hexagonal, liquid crystal. The hexagonal liquid crystal is viscous and so is more resistant to being forced out of the solid phase and onto the surfaces of the soap candles in the plodder cone.

Less liquid phase on the candles gives better candle-to-candle adhesion and less cracking. Because there is less liquid on the candles, less extra water is absorbed between the candles during mushing (there is less electrolyte, glycerol, and soap to dilute), and there is less inter-candle mushing and less stress when the mush dries.

Soap-to-Water Ratio at Manufacture

In the context of soap properties involving water penetration, it is always better to consider the soap-to-water ratio, rather than the water content percentage or TFM percentage. This is particularly important in comparisons with soaps containing fillers or high levels of nonsoap components. For simplicity, we will consider products containing only soap and water as major components. Higher water content therefore means a lower TFM percentage.

There are competing effects, but in general, for modest increases in water content (up to 3% more water), higher water content means less cracking:

- Higher water = more liquid phase = softer soap = better candle adhesion = less cracking

However, the following are also true:

- More liquid phase = more water penetration = more swelling = more mush = more cracking
- More water = a more dilute liquid phase, possibly with some conversion of liquid crystal to isotropic solution = more opportunity for liquid to wet the candles in the plodder = more cracking

The consensus is that for soap with water content up to about 15%, the dominant factor is the increased softness from the increase in liquid phase volume, leading to less cracking. However, and importantly, the extra water must be included in the soap at the drying stage. If an extra 3% of water is added at a subsequent mixing stage, then it will very likely simply dilute the liquid crystal and form an isotropic solution. This results in poorer mixing, producing inhomogeneity in the soap, and can lead to significantly increased cracking.

At water contents of 15–20%, there is enough water present for almost all of the laurate to move from the solid phase to the liquid phase. The solid phase will then recrystallize from the kappa phase to become substantially the zeta phase—small crystals with good packing. The liquid phase then contains a lot of oleate:laurate and has a viscous liquid crystal structure. The result is that soaps subjected to work energy at more than 15% water content will become hard and tough (and also translucent).

The harder soap will significantly increase pressure in the plodder, forcing liquid phase between the candles, resulting in poorer candle-to-candle adhesion and potentially more cracking. The greater amount of liquid phase forced to the candle surfaces attracts more water penetration to those regions during mushing, giving more swelling and more stress on the structure when the mush dries, again encouraging more cracking.

Note that although mush increases with water content at any moisture level above normal (12%), at much higher moisture contents, say 20% or slightly higher, the mush will decrease if the soap receives sufficient work energy input. This can explain why many laundry soaps have less in-use mush than toilet soaps.

As moisture content increases beyond 20%, water penetration will continue to increase, but mush will decrease. There is no contradiction in this statement. The decrease in mush as moisture content increases over 20% occurs because the kappa and zeta phases are progressively replaced by delta phase. If the long, ribbon-like crystals of delta phase are preformed in a soap, then they will not trap water as it penetrates during mushing. This means less soap swelling relative to soaps containing only kappa and/or zeta phase. Less swelling can outweigh the continued increase in penetration/dissolution loss during mushing, giving an overall decrease in mush and decrease in cracking.

Changing the Titer (Iodine Value) of the Nonlauric Soapmaking Oils

Increased titer (approximately melting point) means decreased iodine value (IV), that is, less unsaturation in the oils.

Again, there are competing effects, but in general, higher IV/lower titer corresponds to less cracking. Increased IV means more sodium oleate and (usually) more sodium linoleate in the oil blend. These soaps are soluble, especially linoleate, and some will be dissolved in water as the liquid phase. An increase in the IV results in an increase in liquid phase volume, a softer soap, better candle adhesion, and hence less cracking.

At constant levels of nut oil (constant sodium laurate), there is a smaller opposite effect, because the greater amount of unsaturated soaps, especially oleate, distributed between the solid phase and the liquid phase has lower solubility than oleate:laurate. This means more water will need to be absorbed to dissolve the extra oleate, and that potentially means more swelling, more mush, more stress when the mush dries, and so more cracking. However, this is a much smaller effect than that from the increased liquid phase volume.

Increased Nut Oil in the Soap Blend

There are competing effects, but in general, increased nut oil means less cracking. More nut oil (up to about 40% in a blend) means there is more opportunity for laurate to move into the liquid phase, resulting in more oleate:laurate formation, greater liquid phase volume, softer soap, better candle adhesion, and less cracking. In addition, more of the very soluble oleate:laurate in the soap means much less water absorption, less swelling, less mush, less stress when mush dries, and less cracking.

On the other hand, more nut oil potentially leads to more residual electrolyte in the soap, hence more in the solution phase, which may migrate to the candle surfaces in the plodder, resulting in poorer candle adhesion and more cracking. In practice, this is a minor effect unless electrolyte levels are significantly above specification.

Increased Glycerol

In general, increased glycerol leads to increased mush and increased cracking. However, the effect is not as big as expected. The same amount of extra water will give a bigger increase in mush.

At high levels, glycerol located in the liquid phase displaces some soap, resulting in a smaller overall liquid phase volume. In contact with water and relative to the soap it has displaced, the glycerol dissolves easily, thus there is less water uptake, less swelling, less mush, and less cracking.

Also, less soap in the liquid phase means a smaller liquid phase, so glycerol at higher levels has a hardening effect on soap. A harder soap means good work energy input, so the laurate will move to the liquid phase, where it forms soluble oleate:laurate, again resulting in less water uptake, less swelling, less mush, and less cracking.

Once again, the effect is not as big as expected, but it is still present—high glycerol does give increased mush and cracking relative to a soap with lower levels of glycerol.

Perfume Effects

Again, there are competing effects, but in general, increased perfume means less cracking. Perfume mainly resides in the liquid crystal phase, increasing the phase volume and therefore the soap's plasticity, which leads to better candle adhesion and less cracking.

Importantly, although the effects of different perfumes vary, higher levels of perfume almost always change the structure of the liquid crystal phase from the viscous hexagonal structure to the much less viscous lamellar phase structure.

In theory, the lower viscosity makes the liquid phase more likely to migrate to the candle surfaces under plodder pressure, giving poorer adhesion and more cracking. This probably occurs in practice, but the softening effect of the hexagonal-to-lamellar change predominates, so that, overall, more perfume means less cracking.

Free Fatty Acids (Superfatting)

Superfatting involves a minimum of 5% free fatty acids (some say 7.5%) and preferably at least 30% nut oil in the overall oil blend. These levels affect various performance attributes of such soaps, notably lather. For the cracking issue, we will consider any soap with free fatty acids greater than 5%.

There are competing effects, but in general, superfatting decreases soap cracking. The liquid crystal phase of soap is highly oleophilic, and free fatty acids will locate in that phase. This will increase the liquid phase volume, giving softer soap, better candle adhesion, and less cracking. Also, free fatty acids will change the structure of the liquid crystal phase from the viscous hexagonal form to the less viscous lamellar form. This will further soften the soap and reduce cracking. All else being optimal, these effects will predominate over any effects from greater mobility of the lower-viscosity lamellar phase leading to reduced candle-to-candle adhesion.

On the other hand, if superfatted soap is processed at too high a temperature, say greater than 35–37 °C, then the liquid phase will contain only a limited amount of laurate soaps. The laurate will be trapped in a solid kappa phase. When the soap is in contact with water, a lot of water is absorbed to try to dissolve this laurate, and when it does dissolve, the kappa phase changes to delta phase, trapping the water onto the bar surface. Thus, there is more mush and more cracking. However, the soap-softening effects will probably predominate.

Electrolyte

More electrolyte gives more cracking. The major effect is that electrolyte will "salt out" soaps from the liquid phase by ionic strength and common ion effects, resulting in less liquid phase volume, harder and less plastic soap, poorer candle adhesion, and more cracking.

In addition, there will be more electrolyte in the liquid phase, and when it migrates to the candle surfaces under the influence of plodder pressure, it will be more effective at reducing candle-to-candle adhesion, also resulting in more cracking.

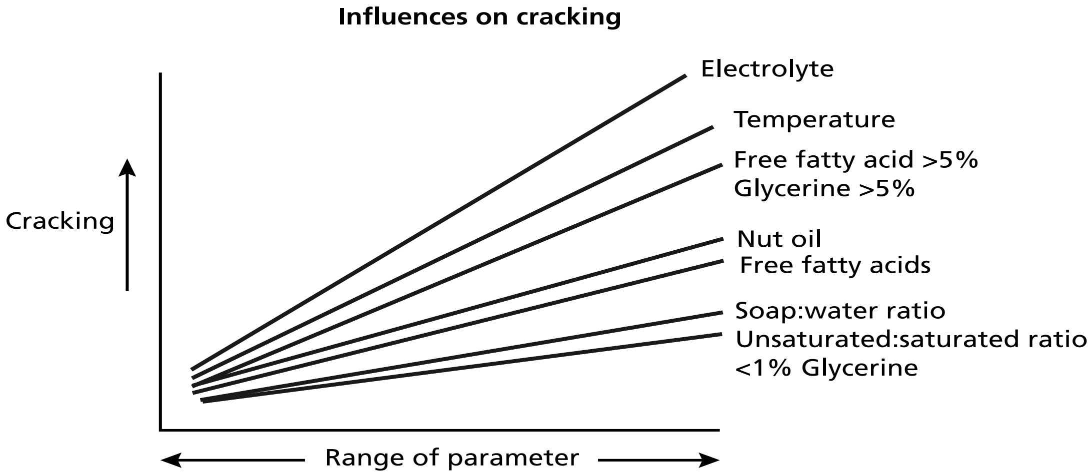
Overall Composition Effects

There are always competing effects, even for an individual composition change. One composition change may introduce another, for example, increased nut oil will almost always increase electrolyte.

In very broad terms, the influences on cracking are as follows:

- Major effects from electrolyte and especially from temperature if free fatty acids are present
- Moderate effects from nut oil level, from low levels of free fatty acids, and from higher levels of glycerol
- Smaller effects from perfume, oil blend IV, and low levels of glycerol

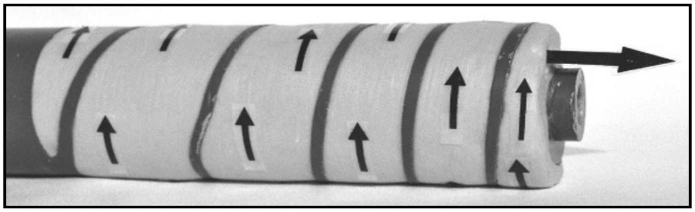
The schematic graph on the next page is a starting point for discussion of the magnitude of effects from different formulation changes. The scales quoted represent the author's experience, but much more work is needed to complete the picture.



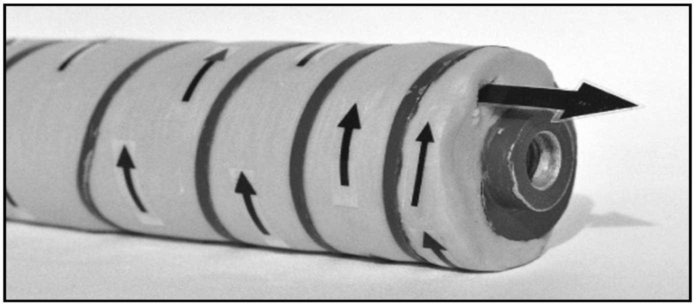
0.4	Total electrolyte	0.8
45	Temperature	35
5	Glycerin >5%	10
10	Free fatty acids >5%	5
30	Nut oil level	15
1	Free fatty acids <1%	0
1.5	Perfume	0
5.2	Soap:water ratio	7.2 = 76–81% TFM
1.2	Unsaturated:saturated ratio	0.7
1	Glycerine <1%	0

Appendix

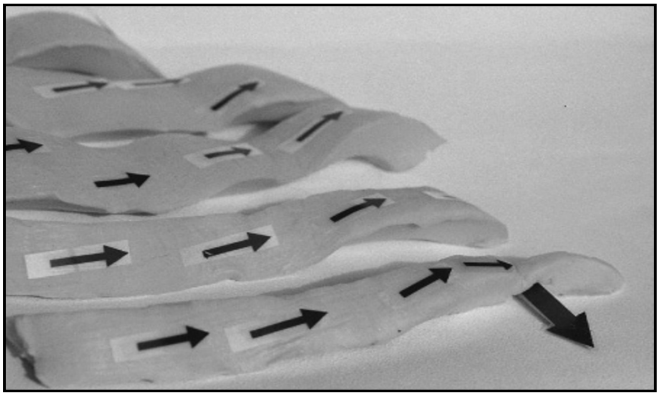
One technique to help visualize soap flow and crystal orientation in a plodder is to remove a soap-filled screw from a plodder and draw lines on the soap surface showing where it was in contact with the plodder barrel wall. The lines should represent where the soap will shear against the barrel wall. On a soap-filled screw they will be perpendicular to the longitudinal axis of the screw and oriented in the direction shown below (if the screw rotates counterclockwise when viewed from the cone end).



A second picture shows a closer view of the shear direction at the point where the soap leaves the screw and enters the cone, and emphasises a sharp change in the direction of soap flow.



While the soap is still warm and plastic, remove it from the screw and open out the piece of soap into one long strip. The lines originally drawn perpendicular to the longitudinal axis of the screw will now be seen as running parallel to the length of the total strip of the soap removed from the screw.



As described in the text, the asymmetric soap crystals will align parallel to the direction of shear indicated by the arrow marks in the photograph. At the point just before the soap leaves the screw flight, the soap will have been subjected to considerable shear.

However, at the point where soap enters the cone, there is a very sharp change in soap flow direction, which implies that soap crystals entering the cone will have a longitudinal axis perpendicular to the direction of soap flow. In the cone, the flow of soap against soap will realign the crystals so that they are again parallel to the direction of soap flow. The realignment process requires energy and is probably associated with the phenomenon known as "work softening."

2 Soap Structure and Phase Behavior

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Introduction

While soap has been used since antiquity, soap production has historically been more of an art than a science. For example, the soap-boiling process, widely used for centuries, manipulated a soap mass around and through various phases with such cryptic names as nigre, middle soap, neat soap, kettle wax, and curd (Vold, et al., 1941).

In the 20th century, however, soap scientists developed a coherent understanding of the structure and phase behavior of soap (Vold, et al., 1941; McBain & Lee, 1943; McBain & de Bretteville, 1942; Buerger, 1942; Buerger, et al., 1942; Buerger, et al., 1945; Ferguson et al., 1942; Ferguson, 1944; Palmqvist, 1983; Zajic, et al., 1968; Dumbleton, & Lomer, 1965; Yang et al., 1987; Vold et al., 1952; Lewis et al., 1969; Tandon et al., 2000; Mantsch et al., 1994; Laughlin, 1994; Small, 1986). As a result, it is now appreciated that the complex behavior of soap systems can be fully explained in terms of the molecular phenomena common to surfactant systems. This chapter will attempt to elucidate the principles of soap behavior in terms of its structure and phases. In addition, the way these soap phases organize relative to one another to form the final bar structure will be discussed in terms of both processing effects and user properties.

Soap Molecular Structure

Soap, commonly defined as the salt of a fatty acid, is the reaction product of aqueous caustic soda with fats and oils from natural sources. As a surfactant molecule, soap contains a hydrophilic head (the carboxylate group) and a hydrophobic tail (the aliphatic chain). This dual character gives soap its ability to dissolve both aqueous and organic phases, its ability to form monolayers at the air–liquid interface (as in foam generation and stability), and its ability to cleanse. The extent to which a particular soap has these properties is determined both by the counter-ion(s) and the aliphatic chain(s) that are present (Piso & Winder, 1990; Murahata et al., 1997; Rosen, 1978).

Depending on the source of the fat or oil used, the distribution of the aliphatic chains can vary as shown in Table 2.1, including chain lengths from C8 to C22 as well as a range of unsaturation, including oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) chains.

Table 2.1 Typical Composition of Natural Oils and Fat

Common Name	Chemical Name	Chemical Formula	Symbol	Tallow	Lard	Coconut	Palm Kernel	Soybean
Saturated Fatty Acids								
Caprylic	Octanoic	$C_8H_{16}O_2$	C8	—	—	7	3	3
Capric	Decanoic	$C_{10}H_{20}O_2$	C10	—	—	6	3	—
Lauric	Dodecanoic	$C_{12}H_{24}O_2$	C12	—	—	50	50	0.5
Myristic	Tetradecanoic	$C_{14}H_{28}O_2$	C14	3	1.5	18	18	0.5
Palmitic	Hexadecanoic	$C_{16}H_{32}O_2$	C16	24	27	8.5	8	12
Margaric	Heptadecanoic	$C_{17}H_{34}O_2$	C17	1.5	0.5	—	—	—
Stearic	Octadecanoic	$C_{18}H_{36}O_2$	C18	20	13.5	3	2	—
Unsaturated Fatty Acids								
Myristoleic	Tetradeconoic	$C_{18}H_{26}O_2$	C14:1	1	—	—	—	—
Palmitoleic	Hexadecenoic	$C_{18}H_{30}O_2$	C16:1	2.5	3	—	—	—
Oleic	Octadecenoic	$C_{18}H_{34}O_2$	C18:1	43	43.5	6	—	25
Linoleic	Octadecadienic	$C_{18}H_{32}O_2$	C18:2	4	4	1	—	52
Linolenic	Octadecatrienic	$C_{18}H_{30}O_2$	C18:3	0.5	0.5	0.5	—	6

Source: Bartolo & Lynch, 1997.

Soap Phase Structure

Solid Soap

As with all pure materials, pure single-chain sodium soap (anhydrous sodium salt of a single fatty acid) will form a solid crystal structure when sufficiently cool.

This structure generally consists of packed bilayers of soap molecules, arranged head-to-head and tail-to-tail. If water is also present, a hydrated crystal structure will form, consisting of packed bilayers of soap molecules with the water of hydration in the region between the packed carboxylate heads.

Solid soap crystals have been probed by X-ray diffraction. The observed diffraction patterns can be divided into two groups: the long spacings that correspond to the perpendicular separation between carboxylate heads in the bilayers (longrange order), and the short spacings that correspond to the lateral separation between parallel aliphatic chains (short-range order), as shown in Figure 2.1. As expected, crystals of pure sodium soaps (anhydrous or hydrated) have a long spacing that correlates with aliphatic chain length. One set of researchers noted four different short spacing patterns in different soap samples. This was taken as evidence of four different molecular arrangements, with four distinct solid soap phases. These solid soap phases were named alpha (α), beta (β), delta (δ), and omega (ω) (Ferguson et al., 1942; Ferguson, 1944). However, another set of researchers concluded that these four were not single phases but were mixtures. They also saw evidence of many more solid crystal phases, including gamma (γ), epsilon (ε), eta (η), zeta (ζ), kappa (κ), mu (μ), and sigma (σ) (Buerger et al., 1942; Vold et al., 1952), leaving soap technologists with a Greek "alphabet soup" of soap phases. While many of these inconsistencies can be attributed to different sample preparation methods (McBain & de Bretteville, 1942; Buerger, 1942; Buerger, et al., 1942; Buerger, et al., 1945), this resulted

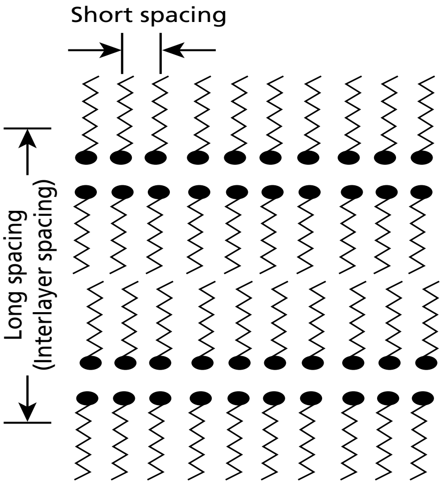

Figure 2.1 Solid soap crystal showing short and long spacings.

in two sets of nomenclature to describe the more common soap phases. A summary of this nomenclature is contained in Table 2.2.

The various types of solid soap phases differ in their degree of hydration, although there is still debate as to whether hydration follows stoichiometric rules or results from a solid solution of soap and water (Buerger, 1942; McBain & Lee, 1943; Perron & Madelmont, 1973; Perron, 1976; Madelmont & Perron, 1976; De Mul et al., 2000). While the existence of multiple solid phases resembles polymorphism, this is not true polymorphic behavior, since these solid soap phases differ in composition.

When soap containing a range of chain lengths is crystallized, solid crystals containing a mixture of chain lengths will form. This is a true solid solution since the molecular composition present in the solid crystals may vary continuously. In addition, multiple solid phases may form and coexist. These solid crystals have been characterized as the same solid crystal phases that form from the pure chain length soaps and water.

It is well known that morphology and hydration affect crystal dissolution behavior (McCrone, 1965; Bernstein, 2002; Grant & Higuchi, 1990). Therefore, it would not be surprising if the various types of solid soap crystals differed from one another in properties related to dissolution, such as lathering or mush properties. However, while such properties have been reported for bars containing various types of solid crystals (Ferguson et al., 1942; Ferguson, 1944; Palmqvist, 1983; Zajic, et al., 1968; Bartolo & Lynch, 1997), the

Table 2.2 Nomenclature for Solid Soap Phases

Buerger Nomenclature (Unilever)	Ferguson Nomenclature (Procter and Gamble)
Eta (η)	Omega (ω)
Kappa (κ)	Omega (ω)
Zeta (ζ)	Beta (β)
Delta (δ)	Delta (δ)

Sources: Buerger, et al., 1945; Ferguson et al. 1942; Ferguson, 1944.

dissolution properties for the single crystals in isolation have never been reported. This is especially significant since commercial soap bars contain multiple components that are divided among multiple phases (as will be discussed in the section on Soap Colloidal Structure), so that the recrystallization of one dispersed solid crystal phase into another solid crystal phase must be commensurate with corresponding changes in the composition and/or phase structure of the continuous phase. While it is tempting to attribute differences in soap bar behavior solely to the type of solid soap crystal present, the effect of changes in the continuous phase must not be ignored.

Liquid Crystalline Soap

A liquid crystal is defined as a class of material that has both liquid- and solid-like properties. Liquid crystalline soap phases can form either when anhydrous soap is heated or mixed with water. These phases are classified as thermotropic and lyotropic liquid crystals, respectively. In either case, the tail portions of the soap molecules become more fluid, resulting in a loss of short-range order, as in a liquid, while still maintaining their long-range order, as in a solid. The various types of soap liquid crystals are discussed in the following sections.

Thermotropic Phases

When anhydrous soap is heated, it passes through numerous phases prior to melting. These phases, called subwaxy, waxy, superwaxy, subneat, and neat II, are thermotropic liquid crystals because their formation is primarily determined by temperature (as opposed to composition), as shown in Figure 2.2. These soap phases have long been recognized by soap boilers, who named all these waxy phases. However, as these phases do not occur in commercial soap bars at temperatures typically encountered, they are of primarily academic interest to soap technologists.

The term "curd phase" that is commonly encountered in soap literature has not been well defined. This term is sometimes used to refer to an anhydrous soap prior to its transition to the subwaxy anhydrous polymorph (Vold, et al., 1941; Skoulios & Luzzati, 1961), as shown in Figure 2.2. In other instances it has also been used to refer to crystal hydrate (Laughlin, 1994).

Lyotropic Phases

A variety of lyotropic liquid crystal phases in a well-defined sequence can form when a surfactant molecule is mixed with water. The generic sequence of these liquid crystal phases with increasing water is shown in Figure 2.3. In soap–water binary systems, however, only two of these phases are apparent. When anhydrous soap and water are mixed and allowed to equilibrate at the appropriate temperature (dependant on chain length and degree of unsaturation), two lyotropic liquid crystalline phases can form: a lamellar liquid crystal phase at lower moisture and a hexagonal liquid crystal phase at higher moisture (Figure 2.4 on p. 41).

The structural transition between the lamellar and hexagonal phases will invariably pass through what is commonly referred to as an intermediate phase. The structures of these intermediate phases remain uncertain and can range from distorted rod-shaped aggregates (Seddon, 1990; Kekicheff, 1989) to pierced lamellar planes (Holmes & Charvolin, 1984; Luzzati et al., 1968; Funari et al., 1992). The intermediate, waxy, and various solid crystal phases are not shown in Figure 2.4, for sake of simplicity.

As depicted in Figure 2.5 (p. 41), the lamellar phase is ordered along one dimension. It can easily be seen that the structure of a lamellar liquid crystal phase is essentially the

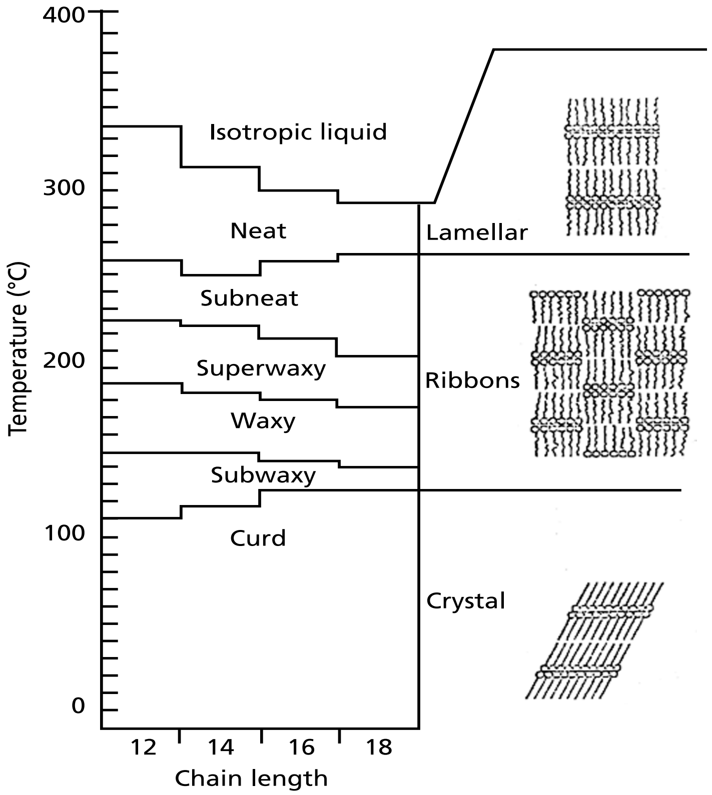

Figure 2.2 Thermotropic phase behavior of sodium soaps.
Skoulios & Luzzati, 1961.

● ***Water rich composition***

↑

- I_1—Normal cubic liquid crystal
- H_1—Normal hexagonal liquid crystal
- V_1—Normal bicontinuous cubic liquid crystal
- L_α—Lamellar liquid crystal
- V_2—Inverse bicontinuous cubic liquid crystal
- H_2—Inverse hexagonal liquid crystal
- I_2—Inverse cubic liquid crystal

● ***Surfactant rich composition***

Figure 2.3 Generic sequence of liquid crystal phases.

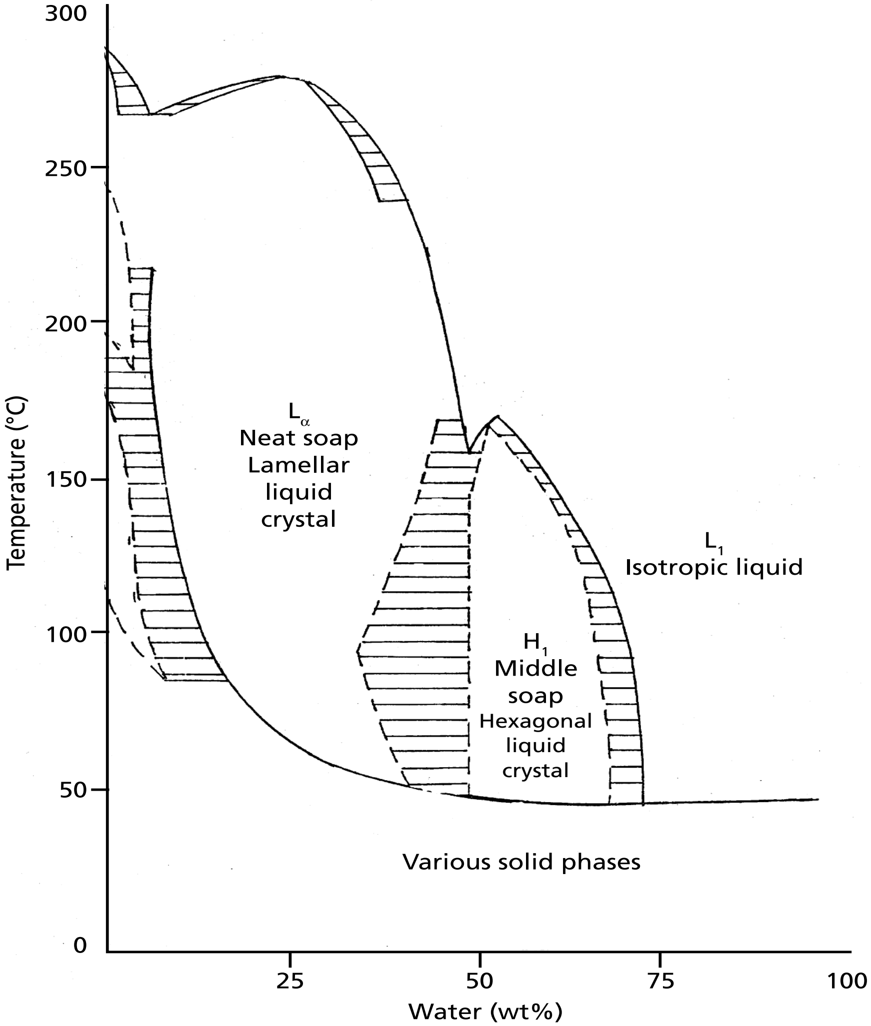

Figure 2.4 Generic binary soap–water phase diagram.

Abbreviations: L—Lamellar liquid crystal; H1—Normal hexagonal liquid crystal; L1—Micellar phase. Palmqvist, 1983.

same as that for a solid soap crystal, except that the hydrocarbon tails in the liquid crystal are in a "fluid" rather than "rigid" state. It is this order in only one dimension that causes the lamellar phase to be the liquid crystal phase with the lowest viscosity.

The soap lamellar phase was regularly observed by the old soap boilers. When boiled soap was allowed to settle, it separated into two layers: an upper layer of a lamellar phase and a lower layer of an isotropic soap solution. Since most of the impurities settled into the lower layer, the lamellar phase was relatively clean, and hence was named "neat soap" (Thomssen & McCutcheon, 1949).

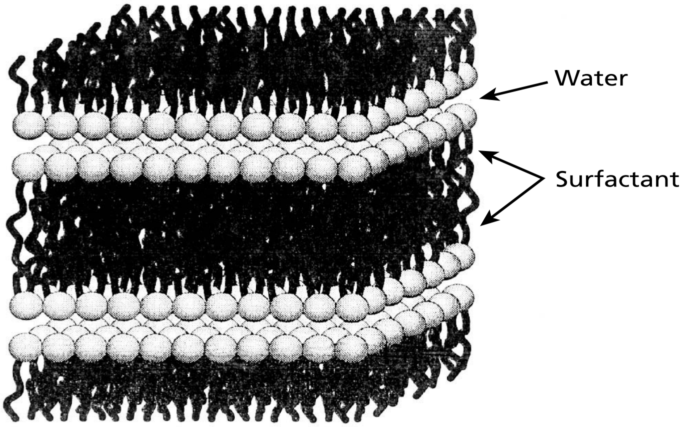

Figure 2.5 Lamellar liquid crystal.
Fennell & Wennerstrom, 1999.

While the lamellar phase can be identified by its low angle X-ray diffraction pattern, it is most easily identified by examination with an optical microscope fitted with cross polarizers. The characteristic optical pattern associated with the lamellar phase is shown in Figure 2.6.

The lyotropic liquid crystalline hexagonal phase consists of close packing of long cylindrical micelles with the soap molecules aligned so that the hydrophilic heads are on the cylinder surface and the hydrophobic tails point toward the center. These structures are

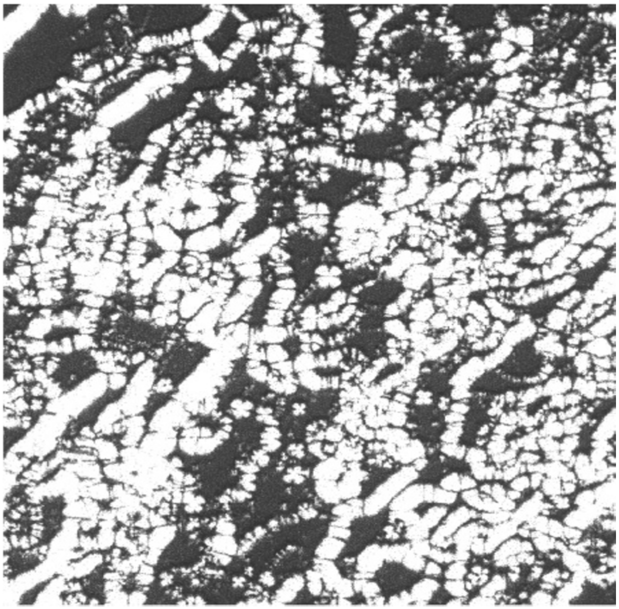

Figure 2.6 Characteristic optical pattern of a lamellar liquid crystal viewed through a microscope fitted with cross polarizers.

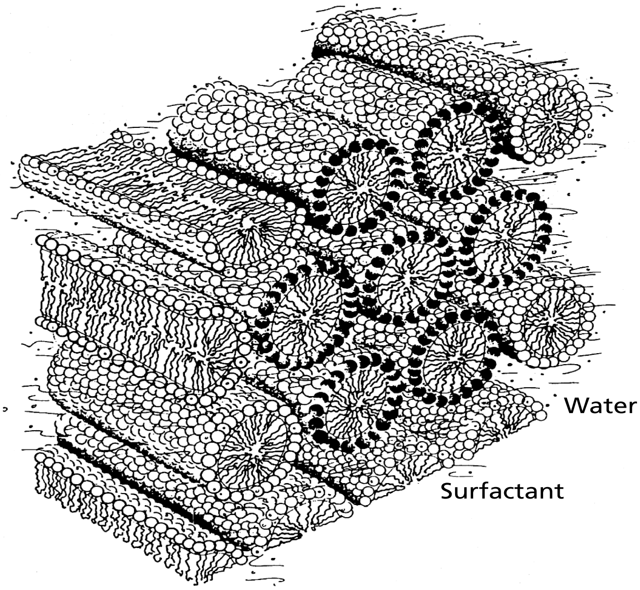

Figure 2.7 Hexagonal liquid crystal.
Rosevear, 1968.

ordered along two dimensions (Figure 2.7). If these cylindrical micelles were to be viewed end on, it would be apparent that they are arranged in a hexagonal pattern with each cylinder surrounded by six others.

On a macroscopic scale these long cylinders form an entangled network, causing the hexagonal phase to have a very high viscosity. Soap boilers knew this phase as "middle soap" because of its location between neat soap and isotropic soap solution in the binary soap–water phase diagram (McBain & Elford, 1926). Well aware of its high viscosity, soap boilers carefully avoided forming middle soap, knowing that once it was formed it would be difficult to process further.

It is well known that soap boilers would keep a ladle of salt on hand to add to boiling neat soap (lamellar phase) to stop the conversion into middle soap (hexagonal phase) (McBain & Lee, 1943). The impact of salt on the transition from lamellar phase, a structure with zero mean aggregate curvature (Figure 2.8), to hexagonal phase, a structure with positive mean aggregate curvature (Figure 2.9), can be explained in terms of its effect on the packing of the soap molecules.

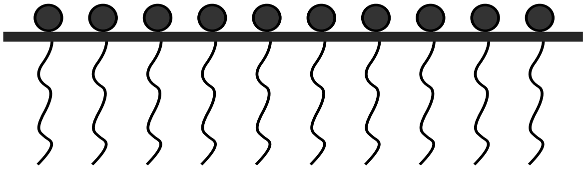

Figure 2.8 Surfactant film with zero mean curvature.
Seddon, 1990.

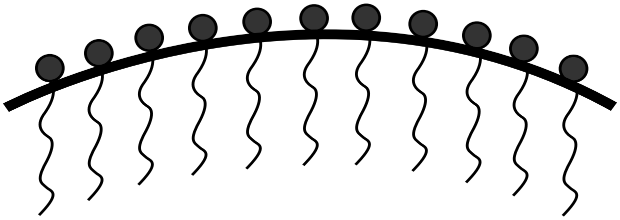

Figure 2.9 Surfactant film with zero mean curvature.
Seddon, 1990.

Aggregate curvature results from the balance of attractive and repulsive forces across a surfactant film. These forces generally consist of head group interactions, interactions at the polar/nonpolar interface, and alkyl chain interactions (Seddon, 1990). More specifically, these include dispersive (Van der Waals), steric, and electrostatic forces (Van Oss, 1991). Depending on the system conditions and composition, it is the interplay between these noncovalent interactions that controls aggregate curvature (Seddon, 1990; Holmberg et al., 2003). The negative charge on the carboxylate group of a soap molecule leads to electrostatic repulsion between adjacent head groups, tending to push them apart and increasing the curvature of the surfactant film, favoring hexagonal phase. However, this effect can be mitigated through electrostatic shielding by the addition of an electrolyte, allowing closer packing of adjacent soap molecules, favoring lamellar phase. Similarly, the addition of uncharged surface active species (e.g., fatty acid or fatty alcohol) can serve to separate the charged species within the packed structures, allowing closer packing of adjacent molecules and thereby favoring lamellar phase. In addition, if the added material is a fatty acid or fatty alcohol, an attractive hydrogen bonding force with the carboxylate head group of soap (Lynch et al., 2001) will also allow for closer packing of molecules.

Figure 2.10 Characteristic optical pattern of a hexagonal liquid crystal viewed through a microscope fitted with cross polarizers.

As with the lamellar phase, the hexagonal phase is most easily identified by examination with an optical microscope fitted with cross polarizers. The characteristic optical pattern associated with hexagonal phase is shown in Figure 2.10.

Isotropic Soap Solution

As with all surfactants, at very low concentrations soap molecules exist in water as monomers. However, as the concentration of soap increases, a point will be reached when the monomers start to form spherical aggregates known as *micelles,* with the carboxylate groups on the surface of these superstructures and the hydrophobic tails all pointed toward the center (Figure 2.11). The concentration where this phenomenon occurs is known as the *critical micelle concentration* (CMC). As the soap concentration increases beyond the CMC, more and more micelles will form. Eventually the micelles will start to distend, and will develop a rod-like shape; at even higher concentrations, they develop a worm-like shape (Figure 2.12). All of these solutions are collectively referred to as *isotropic soap solution.* As the soap concentration is increased further, the worm-like micelles will begin to form a positionally ordered two-dimensional lattice structure having long-range order—the hexagonal liquid crystal phase discussed in the previous section.

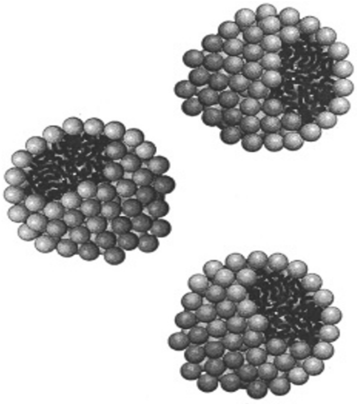

Figure 2.11 Spherical micelle.
Fennell & Wennerstrom, 1999.

The solubility of soap in water is strongly temperature dependent. Solid soap crystals will dissolve to form either monomers or micelles in solution depending upon whether the temperature results in soap solubility that is below or above the CMC, respectively. The temperature at which solubility equals the CMC is known as the *Krafft temperature,* and this corresponds with a rapid increase in soap solubility (Figure 2.13). In soap literature, reference is sometimes made to a Krafft Boundary temperature. This value will typically lie 15–20 °C above the Krafft temperature for a particular soap (Laughlin, 1994). In the case of soap, it typically corresponds to the temperature at which solid soap crystal melts to form hexagonal liquid crystal.

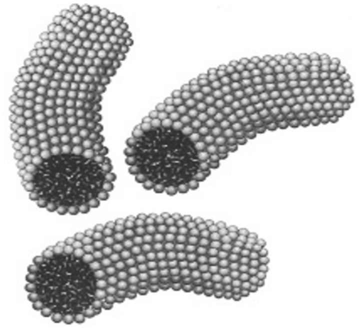

Figure 2.12 Worm-like micelle.
Fennell & Wennerstrom, 1999.

The Krafft temperature of a particular soap is determined both by the counter-ion(s) and the aliphatic chain(s) that are present (Holmberg et al., 2003). For example, for a given aliphatic chain, Krafft temperature decreases as the counter-ion is changed from sodium to potassium to triethanolammonium (Murray & Hartley, 1935). Similarly, for a given counter-ion, Krafft temperature decreases as the aliphatic chain decreases in length and/or increases in degree of unsaturation (Krafft & Wiglow, 1895).

When an isotropic soap solution is viewed through a polarized microscope, the solution will appear completely black, demonstrating the absence of aggregates larger than micelles.

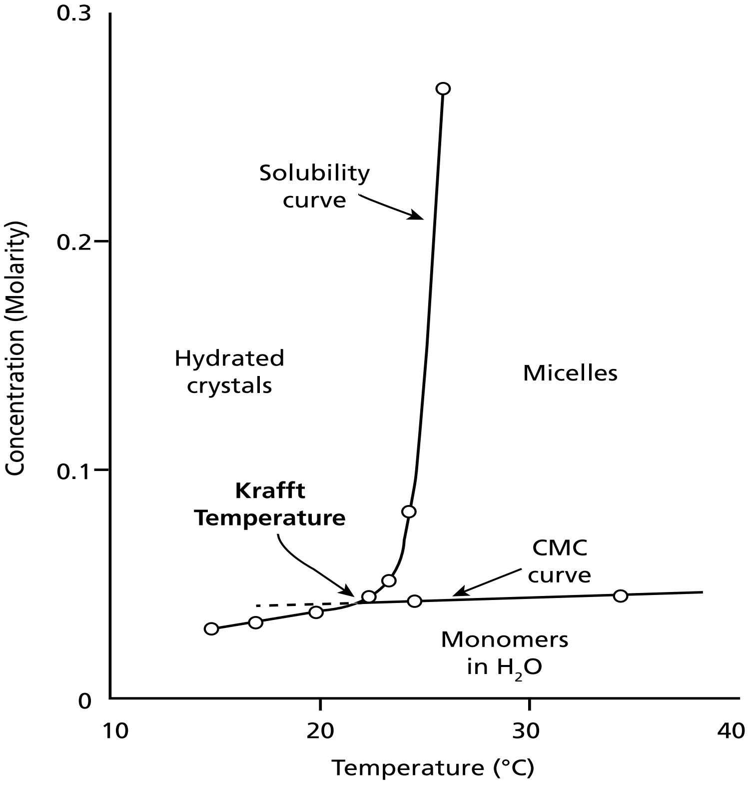

Figure 2.13 Soap concentration versus temperature, showing Krafft temperature. Abbreviation: CMC—Critical concentration micelle. Shinoda, 1963.

Isotropic solution phase was regularly observed by the old soap boilers. As noted previously, by the end of the soap-boiling process, all colored impurities would settle into the lower layer of isotropic soap solution. As a result, this lower layer was darkly colored and hence was termed “nigre” (Thomssen & McCutcheon, 1949).

What is the state of matter of a bar of soap? A soap bar certainly appears solid, yet it can be deformed under sufficient pressure, as demonstrated by the manufacturing processes for commercial soap bars (e.g., extrusion). In reality, a bar of soap may typically contain multiple phases, including various types of solid crystals and liquid crystals, as described previously.

The number of phases that may exist in any system at equilibrium is determined by Gibbs’ Phase Rule (Atkins, 1986). For example, when a soap bar contains the salt of a single fatty acid and water (two components) at room temperature and atmospheric pressure, there can be at most two phases at equilibrium. But as soap is generally made from natural fats and oils, it will typically contain the salts of several fatty acids. This allows the simultaneous existence of multiple phases at equilibrium in a soap bar.

Commercial soap bars contain multiple components divided among multiple phases. This is further complicated by the fact that observed phases may be metastable. For example, the rapid removal of water from neat soap (lamellar phase) during vacuum spray drying precipitates out solid crystals of mixed chain lengths in the form of kappa phase (omega phase with the Ferguson et al. nomenclature [1942, 1944]). The fractions of short-chain saturated soap (C8–C14), long-chain saturated soap (C16–C24), and unsaturated soap (C18:1; C18:2; C18:3) making up this kappa phase will depend on the fat source. However, the fat source will also impact the final equilibrium bar structure. In conventional toilet soap, a mixture of two separate crystal types will form at thermodynamic equilibrium: one crystal type composed of the less soluble saturated long-chain soaps (e.g., C16 and C18), referred to as the *delta phase,* that is dispersed in a continuum of another crystal type composed of the more soluble saturated short-chain soaps and unsaturated soaps (e.g., C12 and C18:1), referred to as the *eta phase.* This configuration of less soluble soaps dispersed in a continuum of more soluble soaps can be compared to "bricks and mortar."

Phase structure notwithstanding, many of the desired properties of soap bars require the rapid dissolution of the more soluble soap components. Significantly, water can more easily interact with the continuous phase in a soap bar than with the dispersed phase. Hence it is desirable for the more soluble saturated short-chain soaps and unsaturated soaps to be in the continuous phase (i.e., in the equilibrium state) not the metastable state.

Mechanical work (shear and extensional flow) during soap finishing (intensive mixing, milling, and plodding) provides the surface renewal to facilitate the migration of molecules to their equilibrium phase through recrystallization. Thus, variations in soap-processing conditions will lead to macroscopic soap property variations, either through changes in the extent to which the actual phase structure is able to migrate to the equilibrium state (determined by the quantity of mechanical work), or through changes in the equilibrium state itself (determined by the process temperature and water concentration).

This transformation toward the equilibrium state can be monitored by changes in the low- and wide-angle X-ray diffraction patterns of the solid crystal phases, or by differential scanning calorimetry. Taking kappa phase soap through a soap-finishing line redistributes

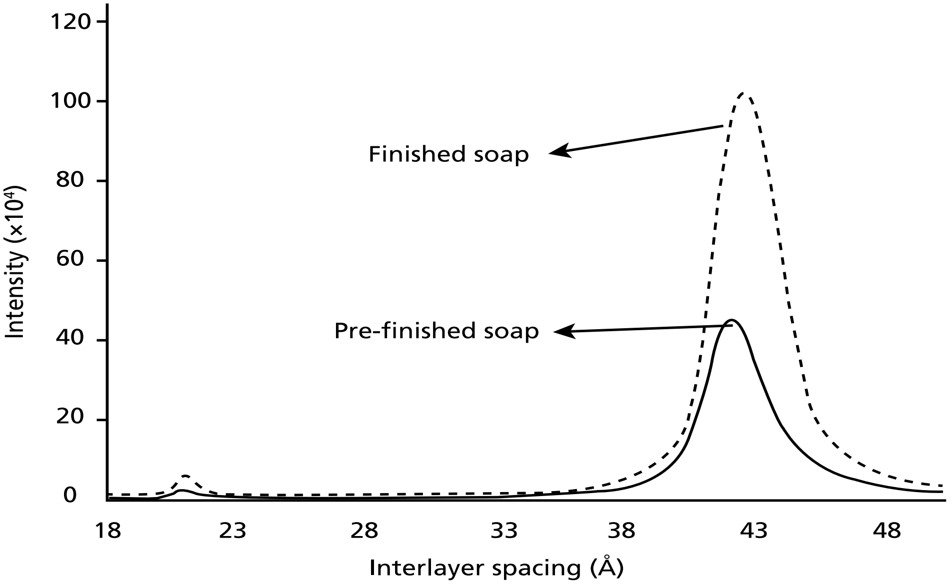

Figure 2.14 Low-angle X-ray pattern of soap, pre- and post-finishing.

the composition of these solid crystal phases, as is evident from the peak broadening and upward shift in the interlayer spacing in the low-angle X-ray pattern (Figure 2.14). Since the long spacing for all solid soap crystals of typical commercial soap blends exists within the range of 40–45 Å, the broadened primary peak for the finished soap in Figure 2.14 reflects the presence of a second solid soap crystal at a slightly higher long spacing. This change corresponds to a transition from the metastable kappa phase to the equilibrium mixture of eta and delta phases.

Corresponding changes in the wide-angle pattern and in the Differential Scanning Calorimetry trace are shown in Figures 2.15 and 2.16, respectively. In each case, a finished soap produces sharper peaks than an unfinished soap because the mixture of eta and delta phases is more ordered than the mixed-chain-length kappa phase.

Superfatted Soap

Commercial soaps may occasionally be formulated to contain excess or free fatty acids, and are then commonly referred to as "superfatted" soaps. While free fatty acid was originally added to soap to ensure the absence of unneutralized caustic soda, properly formulated superfatted soap bars have been observed to produce a high volume of rich dense lather (Piso & Winder, 1990; Bartolo, & Lynch, 1997). This may ultimately be traced to the impact of fatty acid on soap bar structure and phases.

The strong hydrogen-bonding interaction between the carboxylic acid group of the fatty acid and the carboxylate head group of the soap (Lynch et al., 2001; Lynch, 1997) gives rise to acid–soap complexes that may exist as solid crystals. While these complexes appear to form in definite stoichiometric ratios (Lynch et al., 2001; Lynch, 1997; Lynch et al., 1996), the question arises as to whether these complexes are thermodynamically stable states or are "kinetically" frozen states that arise as a consequence of the preparation method. Constructing an equilibrium binary phase diagram of an acid–soap complex is problematic due to the inability of the mixture to equilibrate rapidly in the solid state

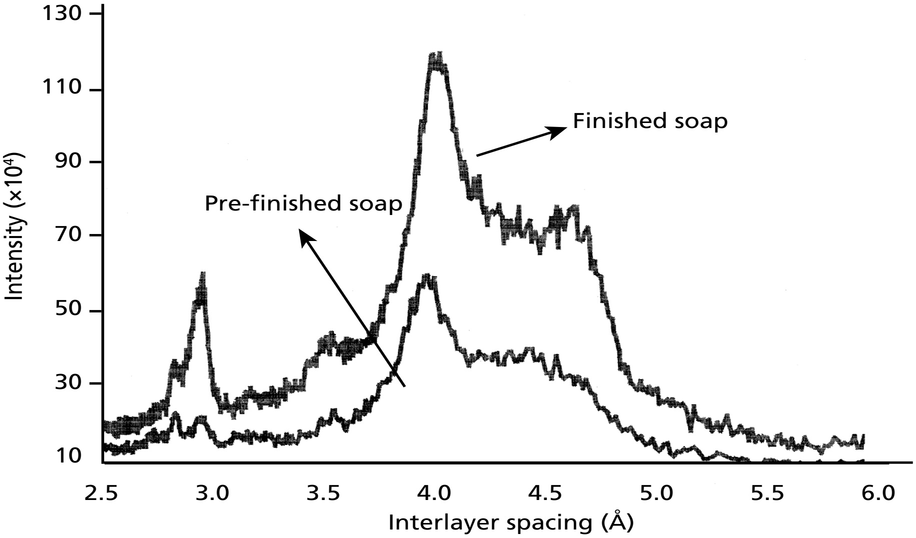

Figure 2.15 Wide-angle X-ray pattern of soap, pre- and post-finishing.

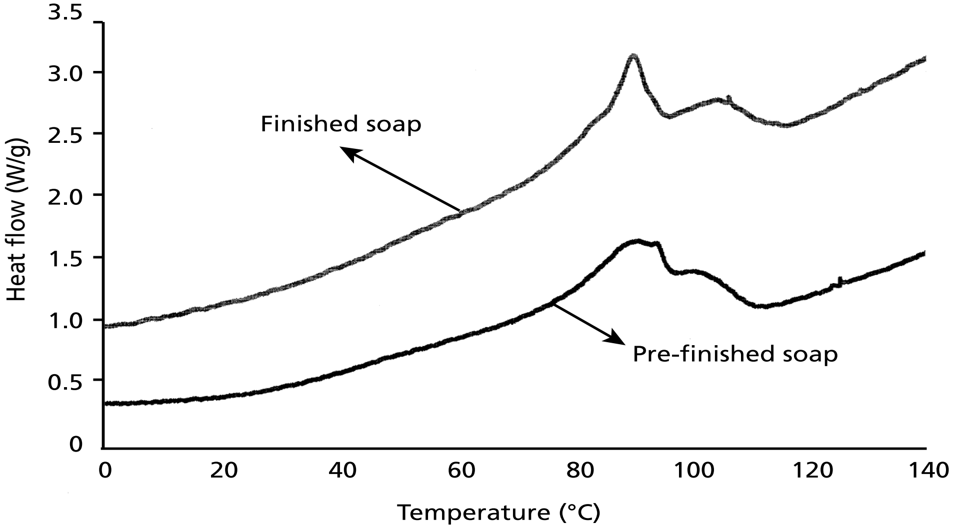

Figure 2.16 Differential scanning calorimetry trace of soap, pre- and post-finishing.

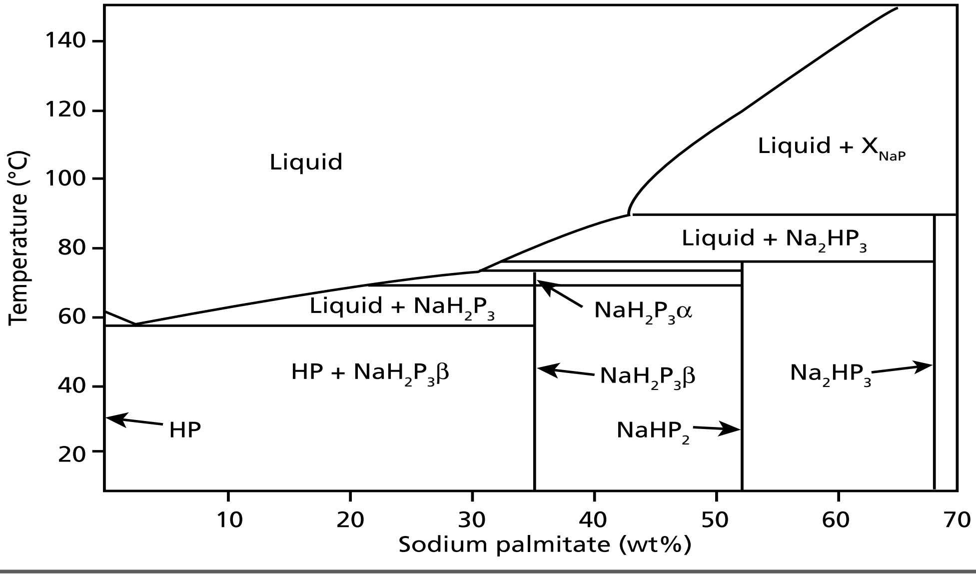

Figure 2.17 Binary acid–soap phase diagram for palmitic acid-Na palmitate.

Abbreviations: HP—Palmitic acid; NaH2P3 —Molecular complex of one molecule sodium palmitate and two molecules of palmitic acid (α and β are polymorphs); $NaHP_2$—Molecular complex of one molecule sodium palmitate and one molecule of palmitic acid; Na_2HP_3—Molecular complex of two molecules sodium palmitate and one molecule of palmitic acid; X_{NaP}—Sodium palmitate crystal. Lynch et al., 1996.

(Lynch et al., 2001; Lynch, 1997; Lynch et al., 1996; Kung & Goddard, 1968). Attempts to resolve some of these issues by careful sample manipulation resulted in a slight revision to the binary phase diagram of Na palmitate–palmitic acid first reported by McBain (McBain & Field, 1933), which is shown in Figure 2.17.

When water is added to a fatty acid–soap system, a rich variety of liquid and liquid crystalline structures will form (Cistola & Small, 1986; Cistola et al., 1988). The temperature at which the different types of structures can form will depend on the nature of the hydrocarbon chain and the degree of unsaturation of the fatty acid and the soap, the ratio of fatty acid to soap, and the amount of water. Figure 2.18 is an illustration of types and expected locations of the various phases in a fatty acid–soap–water ternary phase diagram. It should be noted that this ternary phase diagram describes the general behavior of all fatty acid–soap systems consisting of a single chain length and single degree of unsaturation, provided that system is above the melting temperature of the fatty acid.

What accounts for the superior lathering properties of superfatted soaps? While some have attributed this to the presence of solid crystals of acid–soap within the bar (Bartolo & Lynch, 1997), the lathering properties can also be impacted by the bar's other phases.

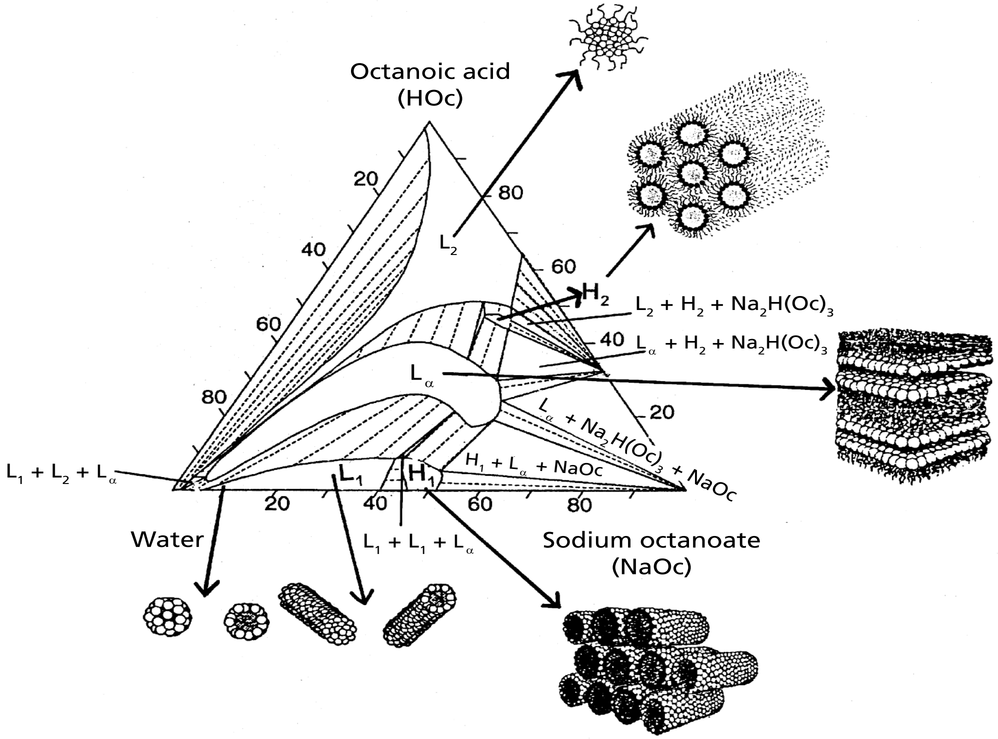

Figure 2.18 Tenary acid–soap–water phase diagram for octanoic acid–Na octanoate water (phase diagram, pictures).

Abbreviations: HOc—Octanoic acid; NaOc—Sodium octanoate; $Na_2H(Oc)_3$—Molecular complex of two molecules of sodium octanoate and one molecule of octanoic acid; H_2—Inverse hexagonal liquid crystal; L_2—Inverse micellar phase. See Ekwall, 1975, 1959; Davis, 1994.

For example, a typical superfatted bar will contain roughly 81% soap, 7% fatty acid, and 12% water, plus minor ingredients. Since this corresponds to a fatty acid to soap ratio of 9%, a single fatty acid–soap system at this composition would be in a multiphase region, where one of the phases would be lamellar liquid crystal (Figure 2.18). A lamellar liquid crystal is similarly present as one of the phases of superfatted soap systems made from blends of fatty acids. The facile interaction between the lamellar liquid crystal and water gives rise to rapid dissolution and hence higher lather volume.

Transparent and Translucent Soap

A soap bar is generally opaque because incident light is scattered by the heterogeneous domains within the bar. This light scattering can be significantly reduced either by matching refractive indices of the various domains, or by sufficiently reducing the domain size of the dispersed phase. Commercial transparent and translucent soap bars capitalize on these phenomena.

Cast Transparent Bars

It has long been known that if certain soap compositions are dissolved in hot ethyl alcohol, they may be cast into molds of the desired shape and allowed to solidify and age for alcohol evaporation, yielding a transparent bar (Cristiani, 1881). It is also possible to make similarly transparent bars using triethanolamine rather than ethyl alcohol, eliminating the need for aging or solvent evaporation to achieve full transparency (Fromont, 1958). These cast transparent bars are sometimes called poured or molded bars.

Cast transparent bars are typically made as a blend of 50% soap and 50% solvent. Depending on the desired bar properties regarding firmness and latherability, the soap blend employed can range from mixtures rich in long-chain saturated soaps to mixtures rich in short-chain saturated and unsaturated soaps (Instone, 1991). The solvent may contain ethyl alcohol, glycerine (or other polyols), sugar, and/or rosin (Murahata et al., 1997; Instone, 1991). The hot soap and solvent solution must itself appear transparent, showing the absence of any solid or liquid crystalline soap phases, or else the mixture will not give rise to transparent bars when cooled (Instone, 1991).

Little has been published on the structure and phase behavior of these systems. Since X-ray evidence indicates the presence of solid soap crystals, it was inferred that these crystals must be smaller than the wavelength of visible light, thereby permitting transparency (McBain & Ross, 1944). More recently it has been noted that the solvents both reduce the quantity of solid soap crystal and limit crystal size (Murahata et al., 1997; Jungermann, 1990). Nevertheless, this does not address the full colloidal structure of these bars.

The manufacture of cast transparent bars is a labor-intensive process since they must be demolded when cool. Hence, these bars have been mass produced only at a premium cost.

Extruded Translucent Bars

It was long noted that ordinary milled soap at high water levels (e.g., 20–30%) appears translucent if the opaque whitening agent is omitted (Ferguson & Rosevear, 1954; Kelly & Hamilton, 1957). While bars with this water level are soft and deform on aging, it was found that replacing some of the water with glycerine both enhances translucency and helps maintain hardness. These compositions achieve translucency both through matching refractive indices of the various domains and by sufficiently reducing the domain size of the dispersed phase.

The difference in refractive indices of the various domains present in a soap bar ultimately stem from the difference in refractive index between soap (n = 1.5) and the solvent, water (n = 1). Addition of co-solvents, such as polyols (glycerine, sorbitol, or propylene glycol), triethanolamine, or their mixtures, can raise the refractive index of the solvent to approach that of soap and improve translucency.

The domain size of the dispersed phase can be reduced by recrystallization. As discussed previously, mechanical work provides the surface renewal to facilitate the migration of molecules to their equilibrium phase. Within the right window of process temperature and water concentration, the equilibrium state for the dispersed phase will consist of small crystallites of zeta phase (beta phase in the Ferguson et al. nomenclature [1942; 1944]) (Ferguson & Rosevear, 1954). Hence, sufficient mechanical work under the right process conditions will also improve translucency. This mechanical work may be delivered to the formulated soap mixture through the use of intensive mixers, roll mills, and/or refiner/plodders. Although they are somewhat less transparent than cast transparent bars, translucent extruded bars can be manufactured on conventional soap-making equipment and hence massproduced at costs similar to that for opaque soap.

Conclusion

As this chapter has shown, a coherent understanding of the structure and phase behavior of soap has emerged over the last century, moving soap production from an art to a science. The complex behavior of soap systems can now be fully explained in terms of the molecular phenomena common to surfactant systems. Nevertheless, some questions involving soap systems persist. Some of these questions are of academic interest, such as those involving the behavior of solid soap at very low water levels. Other questions are of industrial interest, such as those involving the influence of a particular set of process conditions on soap bar properties. No doubt continued study will shed further light on the answers to both types of questions.

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3 Formulation of Traditional Soap Cleansing Systems

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Introduction

This chapter discusses soap base compositions, including a brief historical perspective on traditional soap and matrix effects which may affect the formulation process. Typically, any saponifiable oil can be made into soap, and the characteristics of the end result are dependent on the type of oil used. Traditional soap consists of sodium or potassium salts of triglycerides and fatty acids, notably from beef tallow, coconut oil, and palm kernel oil, and to a lesser extent from such oils as grape seed, sweet almond, rice bran, and others. Varieties of soap include transparent, opaque, and translucent soaps, and specialty bases such as shaving, nonmarring opaque, cream/paste, and powdered soaps. Since the production of these bases is well documented in the literature, they will not be discussed further in this chapter (Chambers et al., 1990; Chambers & Instone, 1990; Davidsohn et al., 1953; Dawson & Ridley, 1989; Deweever & Carrol, 1975; George & Serdakowski, 1987; Joshi, 1985; Jungennan et al., 1988; Nagashima et al., 1981; O'Neill et al., 1974; Swern, 1979; Thomsenn & Kemp, 1937; Verite & Caudet, 1981; Wood-Rethwill et al., 1989; Woolatt, 1985).

The formulation of soap bars has become more complex over the years due to an ever-increasing number of soap bases that incorporate more and more additives. The "green" and "natural" market segments have led to soap products with new materials. Also, consumers have become more accustomed to multifunctional products offered by the cosmetic industry, including conditioning shampoos, antiperspirants, sunscreens, lotions, and creams. Traditional soaps were designed for cleaning skin and clothes, but as time passed, soaps came to be used as a delivery system for perfumes and superfatting agents. Today, the cleansing aspect seems almost secondary to the effects of the various additives that are delivered through the soap system. The *2014 International Cosmetic Ingredient Dictionary and Handbook* published by the Personal Care Products Council (PCPC), lists over 21,000 monographs of INCI names as well as 3,000 suppliers and 68,000 trade names reportedly used in cosmetic applications (Nikitakis & Breslawec, 2014).

In recent years there has been a significant increase in consumer demand for natural, organic and sustainable personal care products. The natural sector has shown double-digit growth annually since 2007. In 2014, the segment showed nearly 30 billion in global sales (GCI Pub., 2015). Many consumers feel synthetic chemical ingredients are inherently harmful and believe natural materials are safer. Because of the Internet and other media sources, today's consumers are better informed requiring ingredients that are ethically sourced and sustainable. Unfortunately, no laws exist at this time to regulate “natural” personal care products, and there is no universally accepted definition of “natural.” In the past, the inclusion of a few plant-based ingredients would satisfy natural consumers; today, the consumer is requiring all-natural ingredients with the function and efficacy of synthetic products. Formulators have a growing palette of natural raw materials to replace traditional synthetic materials; however, the difficulty for the formulator at this time is that not all high-performance synthetic actives have natural equivalents.

As with any drug or cosmetic product, matrix effects must be considered when developing soap formulas. Among these are additive–base interactions, pH effects, additive–additive interactions, fragrance effects, and processing effects. Any combination of these effects may influence the physical and aesthetic characteristics of the final product. Sometimes it is difficult to predict the consequences of matrix effects, and only with time and experience does the formulator begin to understand these interactions.

Additive–Base Interactions

These can occur when acidic compounds are added that may interact with the soap base by changing its physical or chemical characteristics. With enough acidic material, alkaline soap bases may break down into fatty acids, which renders the soap ineffective. This may not be immediately noticeable because the soap base does not have sufficient water to behave like a solution, but it can occur over time after processing and storage.

pH Effects

Most stability problems arising from pH effects occur with additives in traditional soaps, as opposed to cosmetic and personal care products, which have an acidic pH. Certain compounds, including some quaternary compounds and fragrance ingredients, are unstable under the alkaline pH conditions found in traditional soaps. Also, some OTC active ingredients, such as salicylic acid and benzoyl peroxide, are most stable in combo systems, which have a neutral to acidic pH.

Additive–Additive Interactions

Additive–additive interactions are similar to the additive–base interactions mentioned earlier, and the two are handled in the same manner.

Fragrance Effects

Fragrance effects develop from fragrance compounds, such as aliphatic and aromatic acids, esters, ketones, and glycols. These compounds can profoundly affect the processing characteristics by increasing the softness and tackiness of the soap or, in the case of translucent or transparent soaps, altering the optical clarity. Fragrance diluents or solvents appear to soften and/or cloud transparent soaps, making an already difficult base even more difficult to work with. These include certain glycols, diethyl phthalate (DEP), and dipropylene glycol (DPG). Also, vanillin is known to cause severe browning in soaps due to chemical reactions in the alkaline pH range. Some newer ingredients on the market can be added to the formulation or fragrance to retard this effect. Formulators should therefore work closely with suppliers to optimize fragrance selections prior to finalizing the formulation.

In order to ensure proper delivery and stability of the fragrance, fragrance suppliers must be briefed on the types of bases that their fragrances will be incorporated into.

Processing Considerations

Processing must be considered when formulating a product. Process parameters that must be monitored or controlled include temperature, shear, scrap recycle, viscosity, vacuum, die refrigeration and shape, type of equipment, milling versus refining, and plodder speed. Although this subject is beyond the scope of this chapter, it is an essential aspect of a successful product, and it must be given due consideration.

Properties of Soap Bases

Chemical Properties of Bar Soaps

Variations in the primary materials of the base formula influence the chemical properties of the soap. For instance, transparent bases can be made from detergents and fats and oils using combinations of sodium hydroxide, potassium hydroxide, and alkanlolamines such as triethanolamine. Synthetic systems can be plasticized with saturated fatty acids, fatty alcohols, or a combination. The ratio of fats and oils (e.g., 80% tallow/20% coconut oil vs. 70% tallow/30% coconut oil) and the choice of manufacturing process (e.g., continuous, full-boiled vs. semiboiled) also affect the chemical properties. However, the choice of the preservation system is critical to the long-term chemical stability of the cleansing system.

Antioxidants are useful as fat, oil, and fatty acid preservatives. However, when these materials are converted to soap, we have found that chelators provide better protection than antioxidants such as BHT. We have found that as a preservative in traditional soap systems at a pH of 10, chelators provide better protection than antioxidants such as BHT. Additionally, BHT can cause severe yellowing of soap products when stored under certain wrapping and warehouse conditions. It is hypothesized that certain quinones form when BHT reacts with nitrogen-based exhaust products produced by warehouse motor trucks and lifts, which leads to the undesirable yellowing.

Virtually all of the preservatives listed in Table 3.1 are chelators. This is because pro-oxidant metals, such as iron, copper, zinc, and magnesium, have extremely negative effects on soap chemical stability, and therefore need to be deactivated. Pentasodium pentetate and tetrasodium etidronate are particularly effective preservatives for color and odor stability in these systems, and they are often needed at levels below 0.10% for each. Chelators may be most functional when used in combination, depending on the type of metals (i.e., speciation) needing to be chelated. A single chelator may only be effective against certain metals and not at all effective against others. The formulator must be familiar with these properties in order to develop additive packages that are stable and functional.

Physical Characteristics of Bar Soaps

The physical characteristics of the soap bar also influence the amount and types of additives that are incorporated into the final formula. With each formulation, the following important bar characteristics and their parameters should be established in order to generate complete product profiles: wear rate, crack resistance and sloughing, washdown, lathering, color, and odor. Additives tend to influence some or all of these aspects of the soap bar, and the potential for negative impacts on them must be determined prior to production.

Table 3.1 Typical Soap Preservatives

INCI Name	Abbreviations
Chelators	
Diphosphoric acid	HEDP
Tetrasodium etidronate (Na_4HEDP)	Sodium HEDP
Etidronic acid	EHDP
Ethylenediamine disuccinic acid	EDDS
Tetrasodium etidronate (Na_4HEDP)	Sodium HEDP
Pentasodium pentetate	Na_5DPTA (DPTA)
Tetrasodium EDTA	Na_4EDTA
Trisodium EDTA	Na_3EDTA
—	$NaLED_3A$ (surfactant-chelator compound)
Tetrasodium etidronate	Sodium HEDP (Na_4HEDP)
Tetrasodium etidronate and pentasodium pentetate	Sodium HEDP (Na_4HEDP) and Na_5DPTA (DPTA)
Tetradibutyl pentaerythrityl hydroxyhydrocinnamate	
Trisodium ethylenediamine disuccinate	Na_3EDDS
Tetrasodium glutamate diacetate	GL
Citric acid and salts	—
Gluconic acid and salts	—
Antioxidants	—
BHT	BHT

Wear Rate

Wear rate describes the lasting power of the soap bar under use conditions. It is influenced by the solubility of the base, which is determined by the titer of the fats and oils, the type of alkali used, and the amount of water.

For instance, transparent soaps have relatively high wear rates due to the use of high levels of solvents, such as glycols, water, and alcohols, which are needed to maintain clarity. These soaps may also contain a surfactant system that aids in maintaining clarity but has high solubility. This combination tends to let the bar “melt away.”

Crack Resistance and Sloughing

The formation of a film on the soap surface occurs when soap is in contact with water for a period of time or in repeated wet/dry cycles. This causes water to penetrate into the soap, swelling the liquid phase. When the film dries, the liquid phase shrinks. The drying causes a contraction of the film, placing stress on the soap surface and causing cracking in weak structural points in the soap. Wet crack test results show that the addition of coconut fatty acids (CFA) eliminates bar panel, face, and end cracking, whereas a control with no added CFA has severe cracking. Alcohol immersion analysis indicates that the control (no CFA) has large fissures, in the substructure, whereas the bars containing CFA have very small micro fissures indicating a substantially reduced cracking potential. Although bars with 1% added CFA did not demonstrate any wet/dry cracking, they demonstrated larger micro fissures than the 2% and 3% bars. This probably represents the lower boundary of CFA that has a reduction effect on wet/dry bar cracking. It can be theorized that the addition of fatty acids to soap increases the liquid phase volume, increasing the plasticity and adhesion of soap filaments and thus reducing the drainage of more soluble components into water, creating voids. This decreases wet/dry cracking.

Based on the results of an internal study, the addition of 1–3% CFA significantly reduces or eliminates bar soap wet/dry cracking. Other factors such as fragrance/additive type and concentration will also affect the crack potential of soap. It is important that these bars be evaluated for other attributes under in-use washing conditions. For additional information, see Chapter 2.

Washdown

The feel of a bar during use can be determined by a washdown test. This is usually performed at a relatively low temperature, such as 85–90 °F, in order to determine if there is any grit, drag, or sandiness in the bar. Synthetic and combo systems are prone to this problem, as well as formulas containing sodium cocoyl isethionate. Causes include improper processing when the base and bar are made or hard particles in the surfactant system. When a bar is allowed to get too cold during processing or shipping, this can create a potentially unpleasant feel for the user, although grit may disappear at temperatures encountered during normal use. Sandiness may occur in traditional opaque soap bases when excessively dry particles form during the vacuum-drying process. This problem is less prominent in soaps with a relatively high water range, for example 12–14%.

Lathering

Although lathering and detergency are not necessarily related, and foam may actually be just a visual aid allowing the user to see where the product has been applied, consumers associate quick, copious foam with quality and cleaning. Foaming characteristics can be influenced by many factors, including the types and ratios of fats and oils or, in the case of synthetics, the types of surfactants and plasticizers. Many additives that are oily in nature tend to act as defoamers if incorporated at high levels, such as in superfatted bars. Traditional soaps will lather poorly in hard water and seawater, whereas synthetics, if properly formulated, will foam well. Standard foam height tests should be performed when determining the product profile.

Color

Soap bases tend to yellow, so that the color of the final bar formulations will also change. This, coupled with additive and fragrance instability, can produce color variations over a short period of time. Accelerated stability testing in oven, sunlight, and/or fluorescent light can help predict the stability of the system.

A reflectance colorimeter is used to record the color of a sample. This instrument mathematically calculates the color as the human eye sees it. Measurements can be stored in a computer database, enabling the color to be recalled in the future as a reference standard. This method can be used for all types of soaps, including translucent and transparent soaps, as well as for determining the yellowness of soap bases. It is a particularly reliable tool for color characterization. Other, more sophisticated color-measuring devices can also be employed that not only measure color, but also formulate and correct soap batches, thus allowing more precise and efficient color matching.

Table 3.2 Color Additives Subject to Certification (FDA Summary of Colors-March, 2007)

Color Additives	Color Index Number	Use in Cosmetics
FD&C Blue 1	42090	—
FD&C Green 3	42053	Except in eye area
FD&C Red 4	14700	Externally except in eye area
FD&C Red 40	16035	—
FD&C Yellow 5	19140	—
FD&C Yellow 6	15985	Except in eye area
D&C Blue 4	42090	Externally except in eye area
D&C Brown 1	20170	Externally except in eye area
D&C Green 5	61570	—
D&C Green 6	61565	Externally except in eye area
D&C Green 8	59040	Externally except in eye area (0.01% max)
D&C Orange 4	15510	Externally except in eye area
D&C Orange 5	45370	Externally except in eye area Lip products (5% max) Mouthwashes, dentifrices (GMP)
D&C Orange 10	45425	Externally except in eye area
D&C Orange 11	45425	Externally except in eye area
D&C Red 6	15850	Except in eye area
D&C Red 7	15850	Except in eye area
D&C Red 17	26100	Externally except in eye area
D&C Red 21	45380	Except in eye area
D&C Red 22	45380	Except in eye area
D&C Red 27	45410	Except in eye area
D&C Red 28	45410	Except in eye area
D&C Red 30	73360	Except in eye area
D&C Red 31	15800	Externally except in eye area
D&C Red 33	17200	Externally except in eye area Lip products (3% max) Mouthwashes, dentifrices (GMP)
D&C Red 36	12085	Externally except in eye area Lip products (3% max)
D&C Violet 2	60725	Externally except in eye area
D&C Yellow 7	45350	Externally except in eye area
D&C Yellow 8	45350	Except in eye area
D&C Yellow 10	47005	Externally except in eye area
D&C Yellow 11	47000	Externally except in eye area
D&C Black 2	77266	—
D&C Red 34	15880	—
Ext. D&C Violet 2	60730	—
Ext. D&C Yellow 7	10316	—

Table 3.3 Color Additives Exempt from Certification (FDA Summary of Colors-March, 2007)

Color Additives	Color Index Number	Use in Cosmetics
Aluminum powder	77000	Externally including the eye area
Annatto	75120	No restrictions
Beta-carotene	75130/40800	No restrictions
Bismuth citrate	—	Scalp hair dye only
Bismuth oxychloride	77163	No restrictions
Bronze powder	77400	No restrictions
Caramel	Caramel	No restrictions
Carmine	75470	No restrictions
Chlorophyllin-copper complex	75810	Cosmetic dentifrices (0.1% max)
Chromium hydroxide green	77289	Externally including the eye area
Chromium oxide greens	77288	Externally including the eye area
Copper powder	77400	No restrictions
Dihydroxyacetone	—	Externally including the eye area
Disodium EDTA-copper	—	Cosmetic shampoo only
Ferric ammonium ferrocyanide	77510	Externally including the eye area
Ferric ferrocyanide	77510	Externally including the eye area
Guaiazulene	—	Externally except the eye area
Guanine	75170	No restrictions
Henna	—	Scalp hair dye only
Iron oxides	77489 77491 77492 77499	No restrictions
Lead acetate	(Prohibited)	Scalp hair dye only (0.6% Pb w/v max)
Luminescent zinc sulfide	—	
Manganese violet	77742	No restrictions
Mica	77019	No restrictions
Pyrophyllite	—	Externally including the eye area
Silver	77820	Nail polish only (1% max)
Titanium dioxide	77891	No restrictions
Ultramarines (blue, green, pink, violet)	77007	Externally including the eye area
Zinc oxide	77497	No restrictions

Odor

Olfactory evaluation of soap bases and finished soap products is as important as any other measurements of physical characteristics. Consumers tend to view fragrance perceptions as being at least as important as any other product characteristic; therefore, it is important that fragrances be formulated for soap to ensure as much stability as possible. Odor stability can be evaluated under similar conditions as color stability. Trained technicians and odor evaluation panels usually review the results of olfactory tests.

Colorants

The use of colorants very much depends on the type of product that is being produced and government regulations governing the product. Colorants can be divided into three categories:

- Color additives subject to certification (certified additives)
- Color additives not subject to certification (noncertifiable additives)
- Color additives not certified (noncertified additives)

In the United States, these distinctions are used in applying the federal Food, Drug, and Cosmetic (FD&C) Act (US Code of Federal Regulations, Title 21, part 1–99) and the Fair Packaging and Labeling (FP&L) Act, which set forth the definitions and labeling requirements for drugs and cosmetics. Drugs must use certified colors, whereas cosmetics can use certified and noncertifiable colors. Soap is exempt from these requirements, and a product can use any combination of colors, as long as it meets the definition of soap and is designated as such. Resources such as the PCPC dictionary can be consulted to determine acceptable and approved colorants in other countries.

Tables 3.2 and 3.3 (pp. 60–61) list some of the more common certified and noncertifiable colorants. Certified colors are common for drugs and cosmetics, whereas noncertifiable colors are primarily used in cosmetic soaps.

Certified Colorants

Certified colorants (see Table 3.4) may be water-soluble, oil-soluble, or oil-dispersible. They also include the corresponding metal lakes. The solutions or dispersions are typically made in the lab at the 1–2% level, but higher loads of 30–50% may be obtained from vendors who have specialized equipment for grinding and dispersion.

Table 3.4 Common Soap Colorants

Certified Colorants	Noncertifiable Colorants	Certified Colorants	Noncertifiable Colorants
Green 3 (CI 42053)	Caramel	Orange 4 (CI 15510)	Zinc oxide
Red 4 (CI 14700)	Chromium hydroxide green	Red 17 (CI 26100)	
Red 40 (CI 16035)	Chromium oxide greens	Red 33 (CI 17200)	
Yellow 5 (CI 19140)	Iron oxides	Violet 2 (CI 60725)	
Green 5 (CI 61570)	Mica	Yellow 10 (CI 47005)	
Green 6 (CI 61565)	Titanium dioxide		
Green 8 (CI 59040)	Ultramarines (blue, green, pink, red, violet)		

Solubility and dispersion tables should be consulted to determine the optimum concentrations for even, complete dispersal. To keep dispersant and additive levels low, it is recommended that colorants be used at the lowest but most effective concentration possible. Certified colorants tend to have the lowest stability of the three categories, and they are affected by a number of factors, including pH, sun and fluorescent light, heat, and additive interactions. For instance, FD&C Green 3 renders a green color below pH 7 but a royal blue above pH 7. Stability stations should be used to determine the overall color stability in the surfactant system.

Noncertifiable Colorants

Noncertifiable colorants (see Table 3.4) tend to be very stable compounds and are used extensively in cosmetics, eye shadows, mascaras, and facial makeup. In some products they can be used as primary and secondary colorants and can stabilize color drifting previously caused by certified colorants. These compounds should be dispersed or wet out before use to maximize their color value. A dispersion aid, such as a 30–40% potassium cocoate solution, helps disperse these colorants well. The formulator can develop a color by approximating the amount of dry pigment and dispersing the powder in the cocoate solution. “Blooming” can occur, where color migrates slowly into the soap system because of large pigment particles, if the colorant is not dispersed properly or dries out before use. Unfortunately, this can happen over hours or days of production and can cause a blotched color in the finished product. However, there are newer materials on the market that contain predispersed colorants for ease of use.

Opacifiers, such as titanium dioxide, zinc oxide, and bismuth oxychloride, also are used to give uniformity to the color system. Without them, the soap may appear to have various light and dark colored areas caused by compression from processing and pressing operations. Titanium dioxide is offered in both rutile and anatase forms, with the water-dispersible anatase USP grade used most often.

Traditionally, rutile types typically do not give the brightness or the hiding power that the anatase gives. However, there are newer rutile versions whose ability to provide opacity, stability, and brightness appears to be comparable to, or better than, the anatase types.

Noncertified Colorants

In the United States, noncertified pigments are often used in bar soaps that conform to the definition and labeling requirements of soap. These colors tend to be very stable and less sensitive to pH and provide a wide range of brightness and hues. They often are supplied as dispersions with concentrations of 25–50%. Also, only small amounts of these pigments are required to achieve dark colors in most soap bases.

Table 3.5 highlights some of the more common noncertified colorants that are used in soaps.

Natural Colorants

The so-called biocolorants, which reportedly have bioactive properties, are another interesting group of materials. These materials are not true colorants, as defined by the preceding categories, but are typically plant extracts that impart a variety of bright colors to the product. They come in the form of water-soluble liquids and powders, as well as in oil-soluble waxes and powders.

Table 3.5 Common Noncertified Colorants in Soap

Pigment Name	Pigment Type	Color Index Number	Pigment Name	Pigment Type	Color Index Number
Phthalo Blue RS	Blue 15	74160	Quinacridone Magenta	Red 122	73915
Phthalo Blue	Blue 15:1	74250	Napthol Red ITR	Red 5	12490
Phthalo Blue GS	Blue 15:3	74160	Carbazole Violet	Violet 23	51319
Phthalo Green	Green 7	74260	Hancock Yellow G	Yellow 1	11680

Fragrances

Virtually any scent can be created to fit a product profile and marketing concept. All fragrances should be developed to ensure stability and potency for use in a particular soap matrix. Use levels will vary depending on composition, but ranges typically start at 0.25–0.50% for masking purposes and can go as high as 3–4% for prestige fragrance bars.

At high use levels, it is important to use vacuum in the extrusion process to minimize surface bubbling or blistering caused by the fragrance components. With the vacuum system, a very small amount of fragrance will be sacrificed in order to obtain a uniform overall extrusion.

As mentioned previously, fragrances may affect the processing of soaps to the extent that they will not extrude or press (stamp) at the desired rates. This is seen in synthetic and combo systems and, more dramatically, in translucent systems where clarity and firmness are critical. As indicated earlier, two particular fragrance additives used as solvents cause problems in translucent soaps. Dipropylene glycol (DPG) and diethylphthalate (DEP), tend to make translucent soaps sticky to the point where the soap does not extrude or press at all. When these solvents are removed from fragrance formulations, a noticeable increase in productivity can be observed. Certain resinoid compounds used in fragrances may also cloud translucent systems due to solubility and particulate effects. Other components may produce similar effects, which should be investigated through experimentation.

Additives

Most soap products include compounds added to achieve a desired functional and/or marketing position. This has become the prime focus of soap formulators. The *PCPC Cosmetic Handbook* (Nikitakis & Brewlawec, 2014) and *McCutcheon's Functional Materials* (Manufacturing Confections Publishing Co., 2006) contain information on many of these functional materials. We discuss several important categories:

- Emollients
- Humectants
- Moisturizers
- Occlusive agents
- Dermabrasive agents
- Drug components
- Anti-irritants
- Foam boosters
- Miscellaneous compounds

Table 3.6 General Emollient Groupings and Common Ingredients

Esters
Butyl myristate
Cetyl palmitate
Glycerol stearate
Isopropyl myristate
Isopropyl palmitate
Octyl palmitate
Tridecyl neopentanoate
Avocado-oil Peg-8 Esters
Glycereth-7 benzoate
Isostearyl lactate

Ethers
Methyl gluceth-1
Methyl gluceth-20
PPG-10 methyl glucose ether
PPG-20 cetyl ether
PPG-20 lanolin alcohol ether
PPG-20 methyl glucose ether
PPG-20 oleyl ether
PPG-20 myristyl ether

Alcohols
Cetearyl alcohol
Cetyl alcohol
Stearyl alcohol
Propylene glycol

Oils and Oil Type
Castor oil
Jojoba oil
Mineral oil
Mink oil
PEG-glycerides
Petrolatum
Shea butter
Cocoa butter
Sweet almond oil
Wheat germ oil
Olive oil
Grapeseed oil

Polyols
Glycerin
Diglycerin

Lanolin Derivatives
Acetylated lanolin
Lanolin
Lanolin esters
Lanolin alcohols
Lanolin fatty acids
PEG-lanolin
Ethoxylated lanolin alcohols

Silicone Derivatives
Dimethicone copolyol
Dimethicone
Silicone fluids
Silicone quaterium-18
Behenyl dimethicone

Evaluation of additive benefits in soap bases is a difficult task for the formulator. Most often, expert panels evaluate performance and aesthetic perceptions. More sophisticated and highly technical techniques can also be employed, such as measurements of transepidermal water loss (TEWL) and skin elasticity, tracer studies for residual ingredients after rinsing, spectroscopic and fluorescence studies, and human skin models. Kajs and Garstein (1991) review the use of these methods in evaluating cleansing products.

Emollients

Emollients are compounds that are used to impart and maintain skin softness and pliability and to generally improve the skin's overall appearance. Fatty esters, alkoxylated ethers, and alkoxylated alcohols comprise the bulk of the ingredients in this category (Table 3.6). Typical use levels are 1–3%. These compounds are stable under normal bar soap conditions; however, care should be taken to review the physical properties of each of these materials in order to determine the best way to incorporate the ingredients into the base, as well as to identify any stability considerations, such as pH and temperature.

Humectants/Moisturizers

Humectants and moisturizers (Table 3.7) are skin-conditioning agents that increase the moisture levels and moisture-retaining abilities of the skin. Their effectiveness depends on the humidity in the environment. Typical use levels vary widely, from 0.1% to 10%. Dahlgren and coworkers (1987) describe the results of instrumental methods of evaluating glycerin in various surfactant systems, as well as perceived skin benefits. The results indicate that high levels of glycerin provide improved skin feel and softness. Monosaccharides or simple sugars, such as fructose and glucose, darken under alkaline conditions, and this

Table 3.7 Typical Humectants and Moisturizers

Saccharides	Ethers	Alcohols	Polyols	Miscellaneous Compounds	Botanicals
Fructose	Methyl gluceth-10	Mannitol	Glycerin	Acetamide MEA	Aloe barbadensis leaf extract
Glucose	Methyl gluceth-20	Sorbitol	Diglycerin	Hydrogenated starch hydrosylate	Hypnea musciformis extract
Honey	PPG-10 propylene glycol	Propylene glycol	Sorbeth-20, 30,40	PCA	Gellidiela acerosa extract
Lactose	—	Octyl decanol	—	Sodium PCA	Sargassum fillpendula extract
Sucrose	—	Tetradecyleicosanol	—	Urea	Avena sativa (Oat) kernel flour
Xylitol	—	Polyglycerin compounds	—	Silicone quaterium-18	Fruit extracts
Galactoarabinan	—	—	—	—	Essential oils and oil extracts
β-Glucan	—	—	—	—	Nonfat dry milk Cranberry seed oil

process is accelerated by the small amount of free alkali that is present in traditional soap bases. The neutralization of the free alkali by the addition of a fatty acid, such as coconut or stearic acid, helps to reduce the darkening effect. The discoloration will vary depending on the type and the amount of the sugar. Disaccharides, such as sucrose, are relatively stable under mild alkaline conditions. Under humid conditions, water droplet formation or sweating may occur with high levels, 10% or higher, of glycols and alcohols, such as glycerin, sorbitol, and propylene glycol. This is a persistent problem with transparent soaps that employ high levels of multiple humectants that also serve as solvents and solubilizers. This hygroscopic effect appears to be less of a problem with other types of soap systems that employ much lower levels, under 5%, of these materials.

Occlusive Agents

Occlusive agents (Table 3.8) include ingredients that are designed to prevent moisture evaporation from the skin, thereby helping to maintain soft and smooth skin. They typically are lipid in nature and are added to achieve the desired effect in so-called dry-skin products. Use levels are in the 1–10% range. The higher levels may cause extrusion and pressing problems by making the soap excessively soft and sticky, but this can be reduced by incorporating the ingredients in the base-making stage or in the premilling/refining stage prior to extrusion.

Dermabrasive/Exfoliating Agents

Dermabrasive agents work in conjunction with cleansers to remove the outermost layer of stratum cornea by scrubbing, thus producing a smoother feel to the skin. Loden and

Table 3.8 Typical Occlusive Agents

Beeswax
Castor oil
Coconut oil
Dimethicone
Hydrogenated oils
Jojoba oil
Jojoba wax
Mineral oil
Natural and synthetic waxes
Olive oil
Petrolatum
Shea butter
Theobroma grandiflorum seed butter
Cocoa butter
Astrocaryum murumuru butter
Sweet almond oil
Tallow
Wheat germ oil
Hydrogenated soybean oil, hydrogenated soybean polyglycerides, C15-23 Alkane
Hydrogenated Soybean Polyglycerides, and C15-23 Alkane
Dilinoleic Acid

Anders (1990) describe a method to measure the effects of dermabrasive cleansers and have determined that they are perceived to improve skin smoothness.

Natural components, such as bran, loofah, oatmeal, jojoba beads, and various seeds, are popular because they can be blended to achieve a desired look in the cleanser and a desired feel on the skin, and they yield a “natural” product. There is currently a growing concern on the impact of plastic microbeads on our environment. Several states have moved to ban plastic microbeads, and there has been some movement to ban them on a federal level. Many, if not most, companies have already moved to natural or more biodegradable alternatives. There has been a large increase in new natural exfoliants offered to fill this need (Table 3.9). Aside from being sustainable and not harming the environment, these alternatives may offer multifunctional attributes such as humectants, emollients, and moisturizers. The use of new green exfoliant materials in bar cleansing products can be a challenge to the formulator since they may have a tendency to degrade easily or discolor the soap matrix. If a natural component is not needed, polyethylene beads of various sizes and colors can also be used effectively. These agents can be added to the amalgamator process under normal conditions, with some precautions. When using refiners, the screen sizes should be large enough to allow the scrub agents to pass through. Otherwise they will be filtered out. Likewise, when using mills, the milling action should not break down the component into fine particles, which will reduce the scrubbing effect. This can be accomplished through proper gapping of the roller mills and the use of low-shear mills. If this is not possible, then a scrub agent can be added in a postmilling step or possibly in the finish extruder with no screens. This problem occurs mostly with larger-sized natural components, such as loofah and oatmeal, and to a much lesser extent with the polyethylene beads. Finally, mild exfoliation can be achieved using spherical exfoliants, such as polyethylene and jojoba beads, since they tend to roll over the skin. Irregularly shaped material, such as crushed seeds, leaves, and shells, tend to provide a more aggressive effect.

Table 3.9 Biodegradable Exfoliant Types

Polymers	Waxes	Botanical
Polylactic acid	Hydrogenated oils	Crushed seeds
Cellulose	Jojoba esters	Ground shells
Polyhydroxybutyrate	Beeswax	Cellulose
Sodium Polyacrylate		

Drug Components

The drug categories in which bar soaps are most commonly included are the antimicrobial and anti-acne products. In the United States, each drug category is governed by a monograph published by the federal Food and Drug Administration (FDA). Each monograph sets the conditions under which a product in a particular category may be sold. Organizations such as the PCPC and SDA, and others, have been working diligently with the FDA over the last several years to finalize the antimicrobial monograph to include personal-care antimicrobial cleansers as a separate product class within this category.

The formulator should consult the relevant monograph to obtain specific information for a category prior to beginning development work on a product containing a drug component, and such products should be manufactured or controlled according to good manufacturing procedures, since the drugs are subject to FDA auditor inspections.

Over-the-Counter (OTC) Active Ingredients in Soap

Typical soap categories containing OTC active ingredients include antimicrobial and topical anti-acne products. Again, OTC/GMP practices need to be enforced in accordance with current United States and European Union monograph requirements.

Antimicrobial Compounds

The FDA is currently reviewing scientific data from industry and academic sources to establish the safety and effectivness of antimicrobials used in personal care products in-order to establish an Antiseptic Final Monograph. Of the antimicrobials, triclosan and triclocarbon are the two compounds most widely used in bar soaps. Typical use levels are 0.3–1% maximum for triclosan and 1–1.5% maximum for triclocarbon. They are incorporated at the amalgamator stage and may be predispersed or dissolved in a suitable solvent, such as a fragrance, prior to addition. As with all drug products, the soap line should be validated to ensure that the finished product is homogenous and that the proper level of antimicrobial is in the soap. Currently, we find no other viable antimicrobial agent for use in bar soap that is proven safe and effective listed in the FDA OTC Antiseptic Drug Monograph.

Anti-Acne Compounds

The most common approved anti-acne ingredient used in traditional bar soap is sulfur, at 3–10%. Sulfur is stable in both alkaline and acid bases and is normally added at the amalgamator stage and processed under normal conditions. Salicylic acid at 0.5–2% and benzoyl peroxide in the 5–10% range are also approved ingredients, but are used mostly in synthetic or combo bases due to stability concerns. Benzoyl peroxide (BPO) tends to readily undergo homolysis yielding benzoic acid, oxygen, benzaldehyde, and other breakdown products. Trace metals and amines should be avoided as they can accelerate homolysis, possibly by lowering the energy of decomposition.

Anti-Irritants

There are several ingredients on the market for which anti-irritant properties are claimed. Among these are sucrose esters, alpha-bisabolol, lactylates, and ethoxylated vegetable oils. Also, surfactant mixtures incorporating materials such as amphoterics, sarcosinates, ethoxylated surfactants, glucosides, and isethionates can reduce the overall irritancy of the product. Most of these compounds have been evaluated in shampoo systems, in which skin and eye irritation levels are reportedly reduced, but they can also be effective in bar soaps.

The overall mechanisms of action are not fully understood, but they are believed to involve several factors, including binding to or formation of complexes with irritants, blocking sites that are prone to irritation, and prophylaxis that covers the skin and thereby reduces or prevents irritant contact. When adding anti-irritants, a baseline test should be run to determine the effectiveness of the irritant. This can be achieved by several different methods that are currently on the market. The so-called soap chamber test, developed by Frosch and Kligman (1979), and the zein test, as described by Gotte (1966), are in vitro methods that measure the ability of surfactants to solubilize the vegetable protein zein. Newer in vitro methods continue to be developed that utilize human skin factors in benchtop assays and will benefit the formulator in screening various additive packages quickly. There does not appear to be one single test that is an adequate predictor of irritancy. Rather, several testing protocols may be needed to evaluate a soap product or surfactant.

Secondary Surfactants

Secondary surfactants are often used to increase the performance of the bar, resulting in improved skin feel, reduction of irritation caused by the primary surfactant, improved solubility, or improved quality and quantity of the foam. Typically they are added at low levels, under 5%, as an adjunct to the primary surfactant.

Theoretically, most surfactants found in shampoos and liquid soaps may be used in bar soap systems as long as they are compatible with the system and are stable at the bar's given pH. However, most of them are pastes and liquids, which tend to make soap systems tacky, resulting in increased processing problems. This is due not only to their physical state, but also to their tendency to lower the viscosity of soap systems, thus causing softening of the system. Additives and fragrances may complicate the situation, as previously discussed.

Table 3.10 lists several of the more common surfactants that are used in the industry, including acyl isethionates, amphoterics, sarcosinates, sulfosuccinates, and sulfoacetates. These ingredients may be added to the amalgamator and processed under normal conditions. In particular, sodium cocoglyceryl sulfonate has good foam boosting, after-feel, and processing characteristics. When working with powdered surfactants, care should be taken to safely handle dust produced. An alternate method for introducing these additional surfactants is to include them in the base-making process so that they become an integral part of the base. For synthetic and combo bases, these surfactants may be added during the normal compounding process. Additionally, Rieger (1993) has developed an excellent list and overview of surfactant types available to the formulator.

Miscellaneous Materials

Several miscellaneous compounds are commonly used in soap formulations. Optical brighteners are sometimes used to shift the appearance of a product from a yellow tone to a bluer tone. For products labeled as soap, one ingredient, disodium distyrlbiphenyl disulfonate, is particularly effective for this purpose at approximately 0.3% in traditional soap base. Currently this compound is a noncertified colorant in the United States and is not acceptable in products labeled as cosmetics or drugs. However, it is approved in the

Table 3.10 Secondary Surfactants

Type	Example	Chemical Type	Form
Acyl isethionates	Sodium cocoyl isethionate	Anionic	Solid
Acyl isethionates	Sodium cocoyl methyl isethionate	Anionic	Solid
Sulfonic acid	Sodium cocoyl taurate	Anionic	Solid
Sulfonic acid	Sodium methyl cocoyl taurate	Anionic	Solid
Amphoterics	Disodium cocoamphodiproprionate	Amphoteric	Paste
Sarcosinates	Sodium cocoyl sarcosinate	Anionic	Liquid-solid
Sulfosuccinates	Disodium lauryl sulfosuccinate	Anionic	Liquid-solid
Sulfoacetates	Sodium lauryl sulfoacetatess	Anionic	Solid
Alkyl glyceryl sulfonate	Sodium cocoglyceryl ether sulfonate	Anionic	Paste
Alkyl glucoside	Lauryl Glucoside	Nonionic	Liquid
Amine oxides	Cocamidopropylamine Oxide	Nonionic	Liquid-solid
Amine oxides	Lauramine Oxide	Nonionic	Liquid-solid
Amino acid	Sodium Lauroyl Hydrolyzed Silk	Anionic	Liquid
Fatty acid salts	Potassium Cocoate	Anionic	Liquid
Fatty acid salts	TEA Oleate	Anionic	Paste
Alkylamido alkylamines	Disodium Cocoamphodiproprionate	Amphoteric	Liquid-paste
Alkylamido alkylamines	Disodium Lauroamphodiacetate	Amphoteric	Liquid-paste

European Union for use in cosmetics. Color stabilizers have recently been introduced that help reduce color fading caused by photolytic effects.

Sodium benzotriazolyl sulfonate, sodium benzotriazoyl butylphenol sulfonate and buteth-3, tributyl citrate, and bumetrizole are a few examples of such compounds. They can be added at the amalgamator.

Encapsulated products can be useful to the formulator. The challenge in using an encapsulated product in soap products is that the capsule must survive during processing, yet have a small enough particle size to minimize the drag or grit feel after washing. If this is accomplished, ease of processing and the delivery of sensitive materials during washing results in enhanced effectiveness and stability. Recently, United States Patent 6,403,543 (George, 2002) demonstrated the suspension of microencapsulated beads in clear glycerine soap. The beads can contain many of the functional materials that have been discussed. This system not only provides an interesting visual effect, but also isolates the functional material from the surrounding soap matrix, thus offering additional stability.

Herbal extracts have gained increased popularity recently due to heightened consumer awareness of the environment and the subsequent offering of “natural” themes in many product categories, including aromatherapy, spa, and fragrance-free products. Extracts of rosemary, chamomile, sage, and aloe, among others, are often used as masking agents to replace fragrances while imparting whatever skin benefits are claimed for them. The current PCPC dictionary has an extensive cross-index of botanicals in the form of powders, oils, and extracts. As with any naturally derived material, specifications should be developed to ensure acceptable purity and consistency with every shipment. Many botanicals are offered in a standardized version, which gives the formulator a degree of confidence as to the strength of the material. Since some of the components in a natural product are unknown, adequate stability studies need to be performed on all formulations to determine whether there are any color or fragrance issues. For instance, certain phenols and tannins may unacceptably discolor the soap.

Other Traditional Cleansing Systems

Cream soaps and cleansing grains are other types of non-bar cleansing systems that have been developed. The cream products can be viewed as modified combo bars that have a paste-like consistency. These formulations include a combination of traditional soap with synthetic detergents, plus structuring agents and beneficial additives. Colorants and fragrances can be added, as well as special ingredients, such as clays and botanicals. The resulting product is paste-like and generates excellent foaming, cleansing, and after-feel. They can be dispensed in a variety of containers, and when pressurized they provide an excellent mousse product. Cleansing grains are formulated with a powdered soap and/or a detergent cleanser, together with beneficial additives, colorants and fragrances, and flow agents. Liquid additives should be kept at a minimum to ensure that the product flows and dispenses properly. Encapsulating the liquid material in a solid matrix, whereby the liquid is delivered when the product is used, allows a greater amount of liquids. These products offer additional opportunities for the consumer to take advantage of advances in personal-care skin-cleansing additives.

Alternative soap bases can be made from nontraditional oils. These include, but are not limited to, grapeseed, olive, sweet almond, and rice bran oils. When saponified, these oils yield a finished soap that can be extruded and pressed. The resulting soap bars are slightly softer than traditional soap made from tallow or palm oil, but are extremely smooth when used, providing excellent lather and a nice after-feel. The all-vegetable oil components may be attractive for market sectors in spa, aromatherapy, and natural product lines. Standard soap additives, as well as botanicals, can be incorporated into these bases.

In conclusion, the formulator is urged to take a balanced approach when developing surfactant systems. Consideration must be given to base type and function, which dictates acceptable additives for the product category. In turn, process considerations must be addressed in order to efficiently manufacture a quality product. Otherwise, surfactant systems can be overwhelmed as one tries to achieve higher and higher end-product functionality in a world of ever-changing consumer cultures and regulatory policies.

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4 Chemistry, Formulation, and Performance of Syndet and Combo Bars

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Soap is undoubtedly the oldest surfactant and skin cleanser. For thousands of years, soap has been obtained from saponification of oils and fats by alkali, the oldest recipe being boiling animal fats and wood ashes. Soap is chemically defined as the alkali salt of fatty acids. In general parlance, the term *soap* has taken on a more functional definition, by which any cleansing agent, regardless of its chemistry, is considered a soap. This sometimes misleading definition will be further considered as this chapter deals with the chemistry of the synthetic detergents and the soapless soap revolution. Conventional soaps that are alkaline salts of fatty acids are characterized by multiple attributes, such as very good emulsification, detergent, and usage properties, as well as ease of manufacture and low cost.

Conventional soaps suffer from two main disadvantages. Soaps hydrolyze in water and release caustic alkali. This subsequently increases the pH of the alkali retained in soap during manufacturing. The high pH of natural soaps affects the skin's natural acidic protective mantle by changing the skin's pH (originally between 5 to 6.5). Even if the pH is restored relatively quickly after washing, this is probably the main cause of the well-known negative soap effect. Another major disadvantage of natural soap, first perceived during the Second World War, is its behavior in hard or salt water. When water is very hard or contains a high level of electrolytes (such as seawater), the foaming performance and cleansing efficiency of soap are seriously inhibited, if not eliminated, as natural soap forms insoluble and inactive salts in the presence of magnesium and calcium contained in hard water:

$$2\ \mathrm{RCOONa} + \mathrm{Mg}^{++} \rightarrow (\mathrm{RCOO})_2\mathrm{Mg} + 2\mathrm{Na}^{+}$$
$$2\ \mathrm{RCOONa} + \mathrm{Ca}^{++} \rightarrow (\mathrm{RCOO})_2\mathrm{Ca} + 2\mathrm{Na}^{+}$$

In addition, the insoluble salts precipitate on the surfaces of sinks and bathtubs as a gray fatty mass that is unsightly and difficult to remove. Unfortunately, the identical phenomenon happens during skin cleansing, on which calcium and magnesium salts precipitate. The dermatological drawback of this is obvious.

The synthetic surface-active agents (surfactants) do not have these important disadvantages, and it is for this essential reason that they have been used in the manufacture of dermatologically recommended syndet bars, also known as soap-less soaps or alkali-free cleansing bars. Surfactants are also used in combination with soap for the formulation of "combo" (also called "combi") bars. Initially, the surfactants were included as minor ingredients to disperse lime soap, and then as co-surfactants at higher percentages.

Soap pH

Conventional soaps neutralized with caustic alkali (sodium hydroxide) have an alkaline pH between 10 to 11 (Lux, Palmolive, Camay, or Ivory) or between 8.5 to 10, when they are partially neutralized with milder alkali amines, such as triethanolamine (Neutrogena). According to their formulation, the popular combo bars have a pH between 8.5 to 10 when the major cleansing agent is soap (such as Lever 2000, Zest, Nivea Milk Bar, or Satina) or even as low as pH 7.5 when only a small amount of soap is incorporated (Dove, Caress, or Olay).

Pure soap-free syndets have a pH between 5.5 to 7, matching the pH of the skin (i.e., Neca 7, Vel, Eubos, Sebamed, pH 5 Eucerin, or Basis pH). For this reason it is believed that the syndets' impact on the natural physiological skin equilibrium is extremely limited, making it the product of choice for cosmetic and baby cleansing bars. In particular applications, primarily medicated/dermatological, the pH can be even lower, between 3.5 to 5, for example in iodine cleansing bars (such as Neca Polydine) in which the iodine complex is shelf stable only in acidic media. A syndet base has the particular advantage of being the most pH suitable media for such applications. Figure 4.1 shows the pH ranges of the various bars.

Chemistry of Synthetic Surfactants

A surface-active agent is defined as a chemical substance that, even at low concentration, absorbs at the surface, reducing the free surface energy at the interface of any two-phase system, such as gas–liquid, liquid–liquid, or liquid–solid. To achieve this, the surfactants must dissolve in each of the two phases. This is accomplished by the presence of two distinct groups in their molecular structure. In a water–oil system, one group will be easily soluble in water (hydrophilic); the other will be insoluble in water (hydrophobic) but soluble in oil (lipophilic). The balance between hydrophobic and hydrophilic features governs the application of the surfactant as a detergent, wetter, or emulsifier.

A known scale, characterizing the surfactant according to its hydrophilic–lipophilic balance (HLB), was presented by Griffin. According to this system, highly hydrophobic surfactants have low HLB values, starting at 1, whereas highly hydrophilic molecules are given high HLB values, up to 40. Detergents, for instance, have values in the range of 13–15, compared to only 4–6 for water-in-oil emulsifiers.

There are four main types of surfactants, classified by the nature of their hydrophilic head: anionic, cationic, amphoteric, and nonionic. The first three are charged molecules. Anionic surfactants possess a negative charge that has to be neutralized with an alkaline or basic material before full detergency is developed. Cationic surfactants are positively

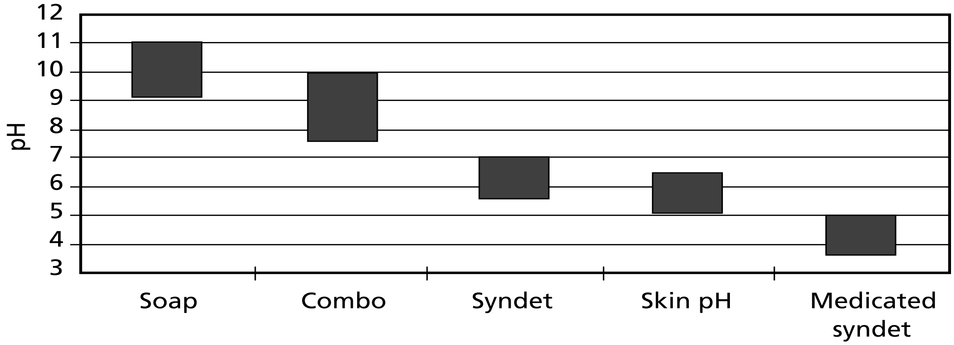


Figure 4.1 Cleansing formulations and pH range.

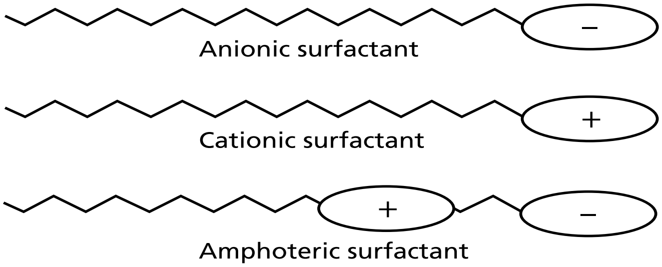


Figure 4.2 Diagram of surfactant types and charge distribution.

charged and therefore have to be neutralized by a strong acid before they can develop surface properties. Amphoterics include both acidic (negative) and basic (positive) groups in their molecules and are positively or negatively charged, according to the pH of the solution. The nonionic surfactants contain no ionic constituents, and have no electric charge (Figure 4.2).

Soap is the simplest anionic surfactant. Since the saponification reaction is a simple hydrolysis of natural materials, soap is often considered a "natural" surfactant. All other surfactants, obtained by many simple or highly sophisticated reactions, are considered synthetic surfactants. Like soap, most surfactants used in personal cleansing bars are anionic. A list of the anionic surfactants (including soap) that are used as active ingredients in cleansing bars is given in Table 4.1.

Table 4.1 Anionic Surfactants Used as Active Ingredients in Cleansing Bars

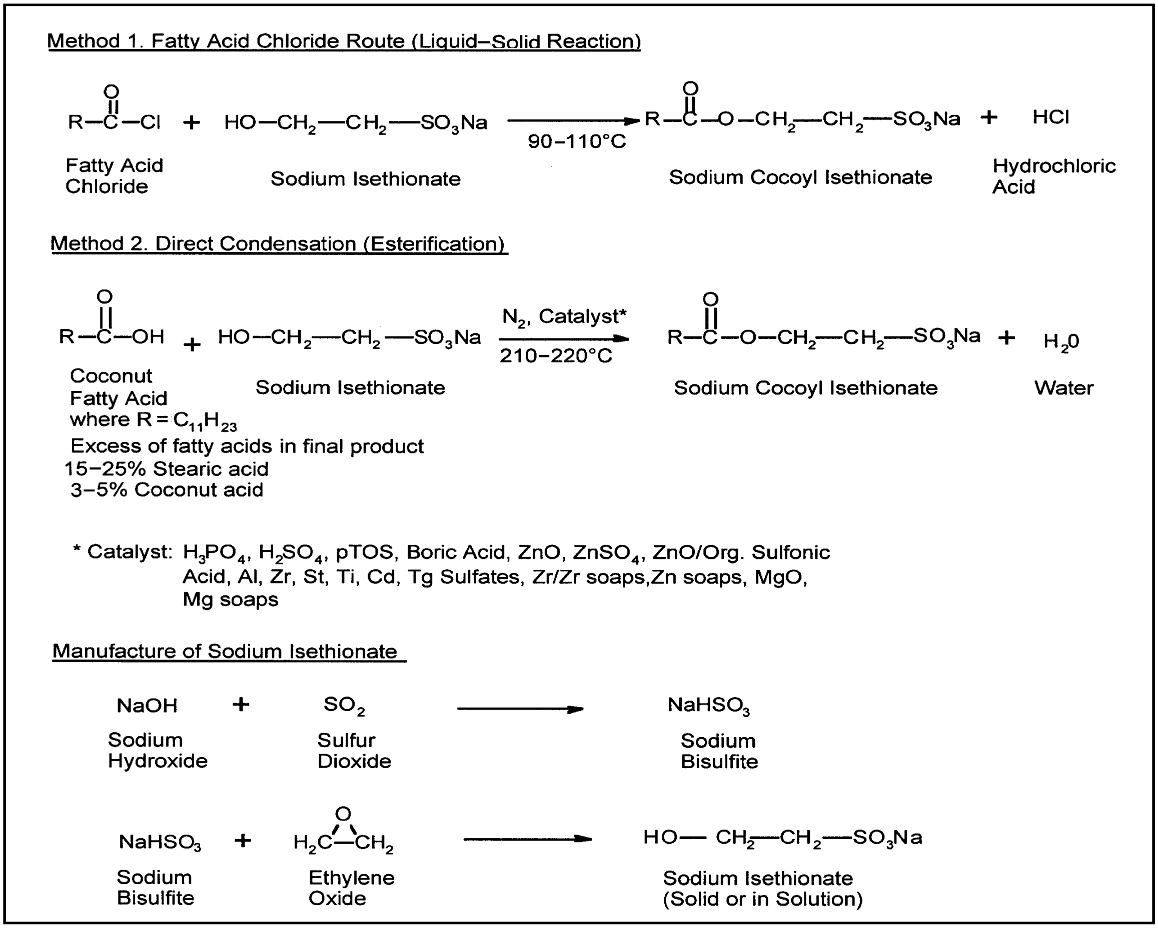
Surfactant Name	Chemical Formula[a]
Sodium carboxylate (soap)	$RCOONa, RCOOMg$
Alkyl sulfate	$ROSO_3Na, ROSO_3K$
Alkyl sulfosuccinate	$ROCOCH(SO_3Na)CH_2COONa$
Amido sulfosuccinate	$RCONHCH_2CH_2OCOCH(SO_3Na)CH_2COONa$
Acyl isethionate	$RCOOCH_2CH_2SO_3Na$
Alkyl glyceryl ether sulfonate[b]	$ROCH_2CHOHCH_2SO_3Na$
Monoglyceride sulfate	$RCOOCH_2CHOHCH_2OSO_3Na$
Linear alkyl benzene sulfonate	$RC_6H_5SO_3Na$
α-Sulfo fatty acid esters	$RCH(SO_3Na)COOCH_3$
Acyl taurate	$RCON(CH_3)CH_2CH_2SO3Na$
Alkyl sulfoacetate	$ROCOCH_2SO_3Na$
Acyl sarcosinate	$RCON(CH_3)CH_2COONa$
Acyl glutamate	$RCONHCH(COONa)CH_2CH_2COONa$
Alkyl ether sulfate	$RO(CH_2CH_20)_{1-3}SO_3Na$
α-Olefin sulfonate	$RCH{=}CHCH_2SO_3Na, RCHOH(CH_2)_{2-3}SO_3Na$
Alkyl ether carboxylate	$RO(CH_2CH_2O)_3CH_2COONa$
Paraffin sulfonate	$RCH_2CH_2SO_3Na$
Acyl lactylate	$RCOO(CHCH_3COO)_{1-3}Na$

[a] $R=C_8$–C_{22}, preferably C_{12}–C_{14} for lathering (mild) surfactant, and C_{16}–C_{18} for less lathering, milder ones.

[b] Also appears as alkoxy hydroxy propane sulfonate.

Surfactant synthesis can be straightforward—getting a surfactant that is easily mixed into the formulation blend. But the more exciting and skillful cost-to-performance formulations are based on "in one pot" in situ manufacturing techniques that, by the nature of their byproducts or reactant excess, will determine the final formulation. The most brilliant example is the Dove formulation that exploited the fatty acid excess, used to shift the reaction equilibrium of sodium cocoyl isethionate (SCI) synthesis, cosmetically presenting it as a moisturizing cream. The SCI synthesis is presented in Figure 4.3.

The old fatty acid chloride route (Daimler & Platz, 1937; Bistline et al., 1971) has been made more economical with many different synthetic and catalytic routes covered by several patents; some are referenced (Anderson et al., 1960; Login et al., 1985; Urban et al., 1985; Gattir & Matthaei, 1975). Special care must be taken to inhibit transesterification between isethionate and stearic acid that are added later (Urban et al., 1985). Lower molecular weight fatty acid reactants volatilized during the reaction are continuously supplied to the reaction mass (Gattir & Matthaei, 1975). Recently, a batch and continuous process was disclosed to prepare soap-acyl isethionate composition with ratios as high as 20:1; it requires a hot



Excess of fatty acids in final product
15–25% Stearic acid
3–5% Coconut acid

* Catalyst: H_3PO_4, H_2SO_4, pTOS, Boric Acid, ZnO, $ZnSO_4$, ZnO/Org. Sulfonic Acid, Al, Zr, St, Ti, Cd, Tg Sulfates, Zr/Zr soaps,Zn soaps, MgO, Mg soaps

Figure 4.3 Synthesis of sodium cocyl isethionate.

(180–200 °F) caustic solution premix of sodium isethionate (Kutny et al., 1991). Catalytic processes introducing new metallic oxides and heavy metal salt catalysts that require temperatures lower than 200 °C, have no yield or reaction rate reduction, improve energy usage, and improve odor and color have been claimed (Day et al., 1993). The synthesis of main sulfonates (LABS, α-sulfo fatty acid esters) and sulfates (alkyl sulfates) by SO_3 sulfonation are presented in Figure 4.4. The preparation of alkyl and alkanolamide sulfosuccinate by sodium sulfite sulfonation is shown in Figure 4.5.

Sulfonation chemistry is well covered in the literature (Davidson & Milwidsky, 1987; Milwidsky, 1985). The hydrophobic chain length, neutralization media, and other parameters govern product suitability in solid-lathering formulations. For isethionates, the synthesis of nearly anhydrous sulfosuccinate in the presence of melted plasticizers and in situ preparation with anionic surfactants, plasticizers, and a small amount of water have been suggested as a straightforward method to manufacture a syndet base (Perla, 1975; Barker et al., 1983). The synthesis of some other surfactants, such as sodium coco monoglyceride sulfate, which had been part of Colgate U.S. "Vel" brand (Weil & Stirton, 1976; Gray, 1959), acyl glutamate (extensively used in Japan), and acyl sarcosinate are illustrated in Figure 4.6 on page 79. Emphasis on chemical stability of the different hydrophylic moieties is important; it is necessary to compare carboxylate susceptibility to alkaline hydrolysis or sulfate hydrolysis under acidic conditions to the chemical stability of the sulfonates.

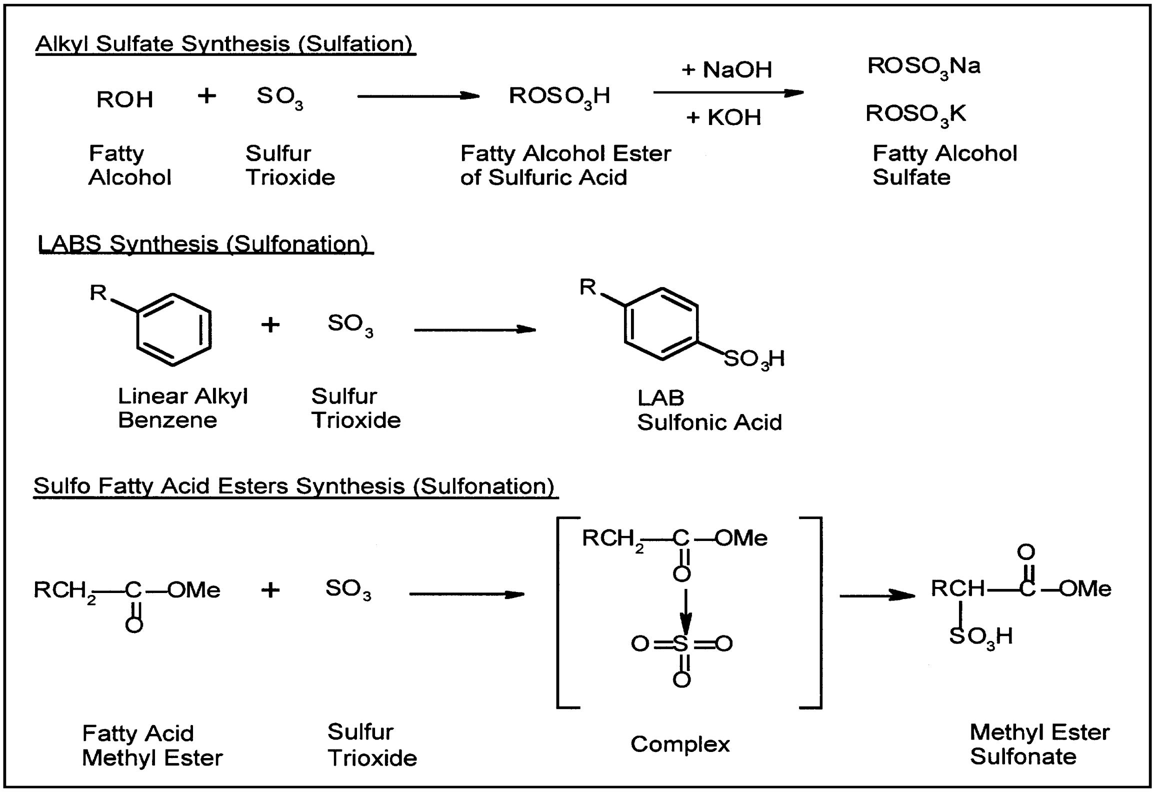


Figure 4.4 Sulfonation/sulfation reactions by sulfur trioxide.

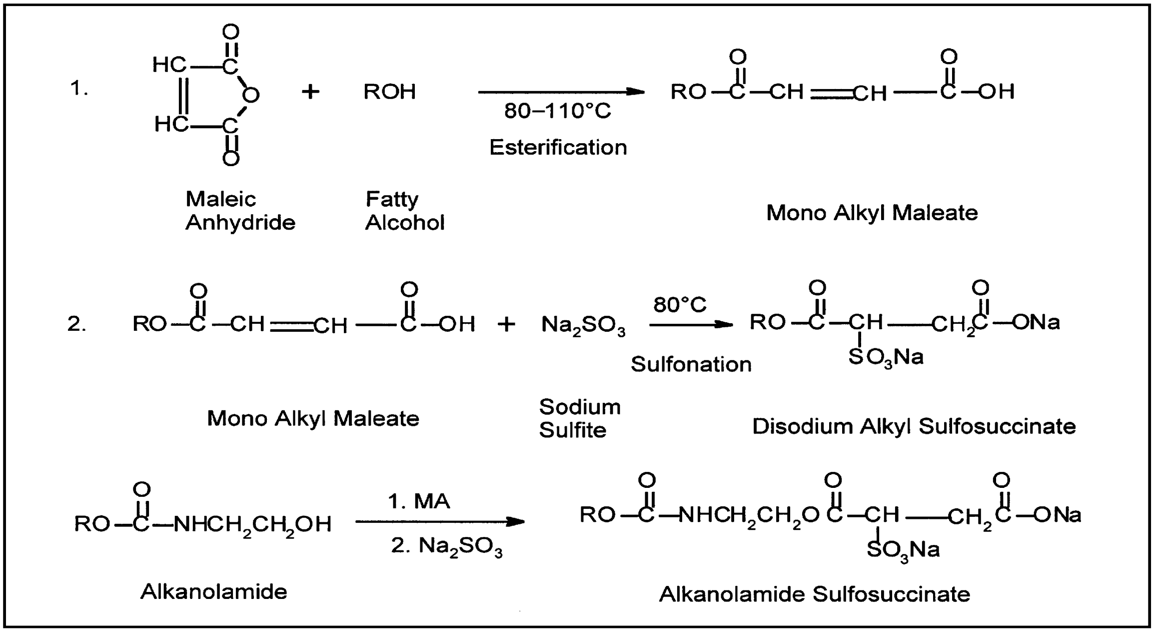


Figure 4.5 Synthesis of alkyl and alkanolamide sulfosuccinate.

Formulation of Cleansing Bars

The list of surfactants presented in Table 4.1 shows a few of the hundreds of synthetic detergents and innumerable plasticizers, binders, moisturizers, and fillers available to formulate syndets and combo bars. The formulation of cleansing bars always involves a skillful combination of scientific thought and almost artistic creativity when selecting appropriate ingredients. The challenge for a soap formulator goes far beyond the manufacture of an effective cleansing agent.

In order to fulfill consumer expectations, a broad range of qualities is demanded of a bar. Social, economic, and psychological demands have advanced along with cosmetic skin care and environmental awareness. This has been followed by substantial cosmetological, dermatological, and technological progress that allows the availability of the sophisticated multifunctional products that is found today. Following these trends, the formulation of syndet and combo bars has become a complex challenge, since final qualities and requirements, including their performance evaluation, are many and occasionally conflict (Table 4.2).

The different test conditions vary based on the test performed, but they have been standardized. Evaluation methods are elaborated according to the company's expertise or official methods and are always aiming for an objective measurement of realistic usage simulation (Wood, 1990; Piso & Winder, 1990). The state of the art in most of the recent patents is based on evaluation by human panels (Redd et al., 1992; Schwartz et al., 1992). These panels, ranging from expert evaluators in the laboratory through small- to large-scale consumer panels, are obvious for sensory evaluation; they are also used extensively for lathering, slipperiness, rinsing, or mush/smear appreciation (Gattir & Matthaei, 1975; Redd et al., 1992; Schwartz et al., 1992).

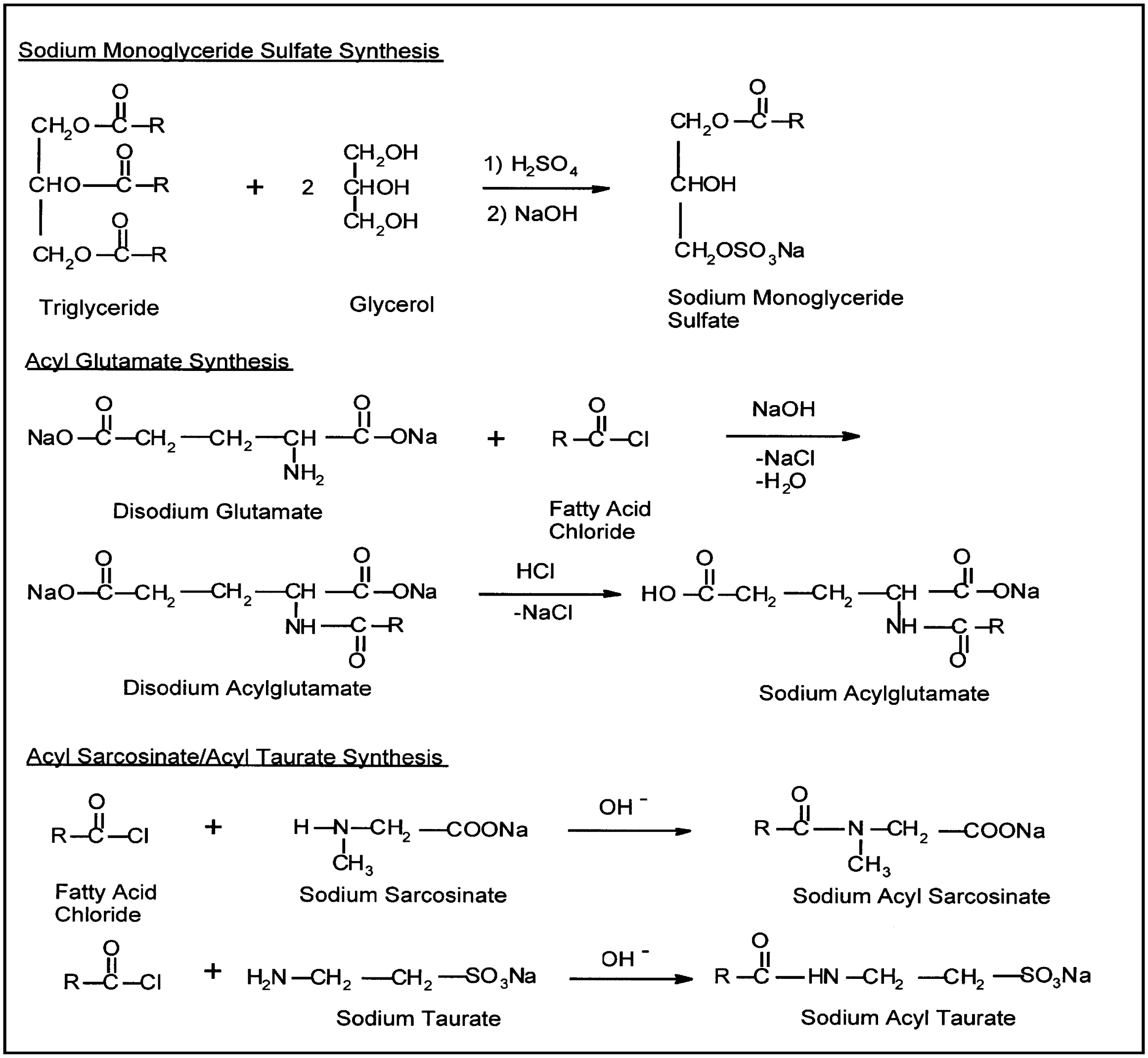


Figure 4.6 Anionic surfactant synthesis.

Table 4.2 Product Performance Evaluation

In addition to cleansing, color, and odor, which were always thought of as main attributes for consumer acceptance, the main bar performance evaluation parameters are:

Lathering (amount, stability, quality, density, speed of formation)
Mushiness/sloughing/smearing
Erosion/wear/use-up rate
Hardness
Rinsability (from skin and bathtub)
Physical stability (wet and dry cracking)
Chemical stability (odor, color, efflorescence)
Skin feel (during and after rinsing/drying)
Lather feel during washing
Mildness/dermatological compatibility
Processability/workability

Processing

Syndet bar processing is more difficult than combo bars and conventional soaps. The syndet products have a very narrow temperature range in which the plasticity permits proper refining and extrusion. Also, due to the sticky and occasionally soft characteristic of the extruded product, stamping rates are adversely affected. There are several types of finishing lines, but for syndet products it is best to have a line that consists of a mixer, simplex refiner plodder, three-roll mill, and a duplex vacuum plodder. A detailed overview of bar soap finishing lines and equipment can be found in Baggini, Nizzero, and Spitz (1990). A main water chiller should supply cooling water to the line, and each machine should have its own independent cooling water temperature control unit. The soap press must have a low-temperature glycol/water die chiller and independent low-temperature controller unit for each stamping die group. A pilot-scale method to produce a syndet bar with long-chain alkyl sulfates for improved processability and bar characteristics is available (Schwartz et al., 1992).

The processing sequence comprises crutching, drying, amalgamating, milling (optionally), plodding, and stamping. A hygroscopicity test to evaluate processability is explained and examples are given. The higher the hygroscopicity, the stickier and more difficult to process a material tends to be (Schwartz et al., 1992).

Product Composition

To achieve all the requirements and properties, a suitable syndet/combo bar is essentially composed from a blend of ingredients as listed in Table 4.3. An ingredient can have multiple and interchangeable functions, for example, binders absorb some of the water, bind the various ingredients together, plasticize the mass, and act as an emollient. A good example of such functionality is high molecular weight polyethylene glycol that is also defined as a structurer (Fair & Farrell, 1995). Moisturizers and emollients are used synonymously.

Table 4.3 Ingredients of Syndet/ Combo Bars

Ingredients	Range (%)
Surfactants	30–70
Plasticizers, binders, emollients	20–50
Lather enhancers	0–5
Fillers	5–30
Water	5–12
Fragrance	0–1.5
Mildness enhancers	0–5
Opacifying agents	0–0.3
Antibacterial, deodorant agents	0–2

Surfactants

Surfactants are primarily responsible for cleansing and lathering. Beside the anionic surfactants already reviewed in Table 4.1, nonionic and amphoteric surfactants used and seldom quoted in the patents are listed in Table 4.4 (Hollstein & Spitz, 1982; Orshitzer & Macander, 1977; Schwartz et al., 1992; Kacher et al., 1993a, 1993b, 1993c; Wilson et al., 1993; Massaro et al., 1995; Medcalf et al., 1987; Pichardo & Kaleta, 1993; Hormes et al., 1995). The nonionics also act as cleansers and plasticizers, but that depends on their HLB values.

A comprehensive list of surfactants, plasticizers, and binders was compiled by Hollstein and Spitz (1982). The state-of-the-art of patent literature, 15 years ago, showed that almost every existing surfactant is a potential active ingredient in syndets. In fact, most of the patents cover the use of almost any surfactant, defining even the potential of using any

Table 4.4 Nonionic and Amphoteric Surfactants

Surfactant Name	Reference
Alkyl polyglucosides	Hormes et al., 1995
Fatty alcohols	Hollstein & Spitz, 1982
Alkyl phosphate esters	Kacher et al.,1993b; Kacher et al., 1993c
Ethoxylated alkyl phosphate esters	Kacher et al., 1993b; Kacher et al., 1993c
Methyl glucose esters	Kacher et al., 1993a; Kacher et al., 1993b; Medcalf et al., 1987
Sucrose esters	Hollstein & Spitz, 1982
Imidazoline amphoterics	Hollstein & Spitz, 1982
Glyceryl monostearates	Hollstein & Spitz, 1982
Protein condensates	Kacher et al., 1993a; Kacher et al., 1993c
Alkyl phenol polyethylene glycol ether	Orshitzer & Macander, 1977
Polyethoxylated fatty alcohols	Schwartz et al., 1992; Wilson et al., 1993
Polyalkylene glycols (PEG)	Massaro et al., 1995
Alkyl betaines	Medcalf et al., 1987
Alkyl sultaines	Medcalf et al., 1987
Alkyl amine oxides	Medcalf et al., 1987
Polyhydroxy fatty acid amides	Pichardo & Kaleta, 1993

"lathering mild synthetic surfactant that lathers at least about as well as the mild standard alkyl glyceryl ether sulfonate" (Redd et al., 1992).

Some compositions are given in Table 4.5, which partly illustrates the present state-of-the-art and has to be seen as complementary to previous lists (Hollstein & Spitz, 1982). During the last few years, newly patented (Ospinal et al., 1999) sulfo methyl esters (SME)

Table 4.5 Surfactant Composition in Combo/Syndets

Composition (%)	Reference
Magnesium soap (5–50%) + any surfactant (20–50%)	Redd et al., 1992
Soap (45–90%) + polyethoxylated fatty alcohol (1–8%)	Wilson et al., 1993
Alkyl glyceryl ether sulfonate (35–80%) + soap (1–25%)	Schwartz et al., 1992
Aldobionamide (20–75%) + polylalkylene glycol (15–65%)	Massaro et al., 1995
Soap (50–90%) + any surfactant (1–20%)	Medcalf et al., 1987
Soap (75–85%) + polyhydroxy fatty amide (1–10%)	Pichardo & Kaleta, 1993
Soap/fatty acid (10–50%) + any surfactant (20–65%)[a]	Kacher et al., 1993a; Kacher et al. 1993b[a]
Soap (70–85%) + alkyl ether sulphate (1–10%), alkyl polyglucosides (0.1–10%)	Hormes et al., 1995
Soap/fatty acid (5–50%) + any nonionic/anionic surfactant (15–65%)	Kacher et al., 1993c
Acyl isethionate (45–70%) + vegetable oil (0.5–2.5%)	Subramanyam, 1995; Subramanyam, 1994
PEG (70–80%) + lauryl sulphate/amphoteric (8–30%)[a]	Moran, et al., 1993 [a]
Sodium lauryl sulphate (70–90%)[a] + binder	Constantine, 1989 [b]
Long-chain alkyl sulfate (18–55%) + soap (1–20%)	Schwartz et al., 1992

[a] Refers to framed/molded bars.

[b] Presented as solid shampoo composition.

have been promoted commercially by Stepan Company (U.S.) for the formulation of combo bars (Ospinal, 1998).

Some patents propose the use of new surfactant molecules. For instance, a nonionic glycolipid surfactant (more specifically an aldobionamide) at 20–75% in a composition structured by 15–65% polyalkylene gycol (preferably PEG of molecular weight 6,000–10,000) and containing no more than 15% fatty acids (Massaro et al., 1995). Unfortunately, the proposed preparation advantages (a renewable raw material source and a no-foam sacrificing structurer) are counterbalanced by the disadvantage of a costly synthesis of n-alkyl lactobionamides (obtained by reacting lactobiono-1.5-lactone with various alkylamines in anhydrous DMF, methanol, or net a lower yield). The choice of surfactants and their proportions not only determines the cleaning and lathering characteristics, but also influences mushiness, plasticity, and skin compatibility.

Formulations

European and Israeli formulations are based mostly on a blend of alkyl sulfates and alkyl sulfosuccinates, reaching about 40–50% surfactant content. The pH of the bar is normally adjusted between 5.5 and 7. It has been found that the potassium salts give much better mushing and plasticity properties than the sodium salts, and there is an optimal K:Na ratio to minimize mushiness (Ramakers, 1992).

The U.S. mass-marketed brands are based on other surfactants. They also followed the soap–syndet concept already patented in the 1940s (soap + LABS + starch) (Hoyt, 1940), followed by nonsmearing bar formulations based on alkyl glyceryl ether sulfonate, sodium/magnesium soaps, and binder (Tokosh & Cahn, 1979). The leader, Dove, is based on fatty acid isethionates, specifically SCI. Since this is an expensive ingredient, the formulation includes about 25–27% fatty acid (specifically stearic acid and a minor proportion of coconut acid) and fatty acid soap, mostly neutralized to a final pH of 7.2–7.5 (Dederen, 1992). The fatty acid presence due to the reaction equilibrium shifting, produces an overall best-performing package, brightly presented as containing 25% moisturizing cream. The product contains some dodecyl benzene sulfonate (1–2%) as a lather enhancer. This surfactant blend reduces the final cost of the formulation but, due to the price of cocoyl isethionate, it is still relatively expensive. SCI bar formulations presented by Ho Tan Tai (2000) according to Unilever patents list a broad range of SCI content of 44–60% and a high electrolyte content of 5% sodium sulfate. The U.S. Dove formulations of the 1990s and the 2008 formulations are presented in Table 4.6.

Table 4.6 Dove Bar Formulations (%)

Ingredient	1992 (USA)	2008
Sodium cocoyl isethionate (SCI)	47–49	48–50
FFA (stearic acid + coconut acid)	23–25	23–26
Soap	7–10	9–11
Sodium isethionate	4–6	4–6
Alkylbenzene sulfonate (LABS)	1–2	—
Cocamidopropyl betaine	—	2–3
Sodium chloride	0.5	0.5–1
Water	4–6	5–6

Since the mildness concept has been strongly advertised by Lever Brothers as an intrinsic property of isethionate bars, a serious change has occurred in bar formulation in Western Europe in the past few years. Products have been reformulated; more expensive isethionate bars, claiming even milder properties, have been introduced. This has changed the surfactant base from alkyl sulfate/disodium lauryl sulfosuccinate (DSLSS) to SCI/

DSLSS base. A typical formulation of Sebamed (Germany) from the late 1990s contained about 25–30% SCI, 10–15% DSLSS, and a blend of fatty acids (C12–C18) and mineral oils of about 30–35%. Similar trends were followed by European syndet base suppliers (Ramakers, 1992, Dederen, 1992).

The drawback of the cocoyl isethionate bar (easily perceived by consumers) lies in its strong, characteristic odor. This odor recalls the coconut source of the fatty acid and needs a higher dosage of fragrance to be covered. It also creates a problem in the fragrance-free hypoallergenic formulations. An interesting contribution concerning this issue should be mentioned (Beerse,et al., 1995). The object of this contribution was to deliver a bar with reduced off-odor and a formulation that is mild to skin and easy to process. These objectives are achieved by using a cleansing bar comprising 10–70% of a sodium-distilled, topped cocoyl isethionate (STCI). The STCI of this invention contains little or no (0–4%) highly soluble acyl groups (C6 + C9 + C10 + C18:1 + C18:2), about 45–65% C12, and about 30–55% C14, C16, and C18. The lack of the more volatile shorter chain odorous hydrophobics, as well as the unsaturated C18 chains is obviously the reason for reduced bar odors. It was also claimed that the STCI formulation allowed the use of higher levels of hygroscopic lather boosters, such as alkyl glyceryl ether sulfonate (AGS), without exhibiting processing drawbacks that would otherwise be experienced with regular SCI. STCI usage also allows the addition of larger amounts of water or liquid ingredients, such as glycerine and vegetable oils (Beerse et al., 1995).

However the significant relevance of these patents (Beerse et al., 1995) to the subject lies in the inclusion of a broad range of functional ingredients that influence soap, combo, and syndet bar properties, such as off-odors, processability, stickiness, brittleness, mushiness, lather quality, and their combinations. The patents become an explicit formulation showcase, which is worth presenting in depth, that allows a close practical insight into the ingredient–performance relationship (Table 4.7). The STCI bars produced with the process are comprised of three key ingredients: STCI, a plasticizing agent, and a binder, in addition to a mild surfactant matrix (Table 4.7) (Beerse et al., 1995). Each will be discussed further.

Other major surfactants used in U.S. formulations are sodium cocoglyceryl ether sulfonate contained in Procter & Gamble's Zest combo bar and in the Olay syndet bar. These last two products also contain SCI. In Japan, acyl glutamate is the basic surfactant in "Mignon," an expensive soapless cleansing bar. Classical formulations of high pH (Davidson & Milwidsky, 1987; Milwidsky, 1985) combo bars, like Lever 2000 and Zest, are described in Table 4.8.

The formulations covered in the 2004 edition of this chapter (Friedman, 2004) have undergone various changes. In the United States, Zest (Aqua Pure) contained the classical Zest ingredient SCGES, but another Zest variant (Tropical Fresh) contains no surfactant at all. Zest in Mexico contains potassium lauryl sulfate as the surfactant of choice. During 2007, some of the Zest bars became regular soap bars without any surfactant. Table 4.8 illustrates the traditional Zest combo bar formula. The Lever 2000 combo bar replaced sodium cocoyl isethionate with sodium methyl 2-sulfolaurate.

A revised list of several suppliers that offer raw materials to formulate syndet and combo bars, as well as fully formulated ready-to-use soap-free or combo bases, is presented in Table 4.9. The unpredictable fast changing soap/syndet/combo bar market during the last 3 years, makes the updating of such a list difficult and sometimes not reliable; even the company's names are difficult to follow. While the list is not current, it has historical value.

For example, Procter & Gamble (P&G) promoted for a short time alkyl glyceryl sulfonate (AGS), and labeled it as sodium cocoglyceryl ether sulfonate (Procter & Gamble,

Table 4.7 STCI Bar Composition (EP 0728186)

Components	Full Range	Typical Range 1	Typical Range 2	Function
STCI	10–70	15–60	20–50	The key to the present invention. It is made from topped distilled coconut fatty acid.
Na-alkyl glyceryl ether sulphonate	0–50	5–30	10–20	Included as a lather-boosting synthetic surfactant. It is made from coconut fatty alcohols. Equivalent synthetic surfactants can be used.
Na-alkyl ether sulfate	0–10	1–8	2–6	A mild lather-boosting synthetic surfactant
Na-cetearyl sulfate	0–40	4–30	8–20	A non-soil load filler and processing aid
Na-soap	0–20	1–15	2–12	A lather booster and processing aid
Mg-soap	0–50	4–30	8–20	A non-soil load filler and processing aid
Fatty acid	0–35	3–25	5–20	A plasticizer
Paraffin	0–30	3–25	5–20	A plasticizer
NaCl	0–5	0.1–3	0.2–2	Provides bar firmness and improves bar smear
Na_2SO_4	0–5	0.1–3	0.2–2	Provides bar firmness and improves bar smear
Na-isethionate	0–15	1–10	2–8	Provides bar firmness and improves bar smear
Water	3–20	4–15	5–10	A binder
Fragrance	0–2	0.5–1.5	0.8–1.2	A binder and improves odor.

Abbreviation: Sodium topped cocoyl isethionate (STCI).

2000, 2001, 2003). AGS 1214 was presented as a surfactant–polymer mixture comprised of (on a dry basis) 72% of an AGS monomer (Table 4.1) and 13% of an AGS dimer, composed of 11% of disulfonate, 1% of chlorosulfonate, and 1% of hydroxysulfonate. The balance contained other molecules, such as 3% of unreacted alcohol, 6% of glyceryl ether (diol), 3% of sodium sulfate, and 3% of sodium chloride, which influence the overall properties of AGS (Procter & Gamble, 2000, 2001, 2003). The product was available as a paste (47% active) or in flakes (75% active). AGS was produced by reacting fatty alcohol with epichlorhydrin, followed by a reaction in a caustic solution to produce an intermediate; this was further reacted with a sulfite mixture and finally oxidized and pH-trimmed to produce the AGS paste (Procter & Gamble, 2000, 2001, 2003).

A typical combo bar formulation using AGS was provided by P&G. The formula included 52% of sodium soap, 17% of AGS, 14% of magnesium soap, 8% of water, 3% of

Table 4.8 Combo Bar Formulations

Ingredient	Zest	Lever 2000	Ingredient	Zest	Lever 2000
Sodium glyceryl ether sulfonate	12–18	—	Soap (tallow/coconut)	50–60	65–75
Sodium cocoyl isethionate (SCI)	—	—	Magnesium soap	5–10	—
Sodium methyl sulfo laurate	—	1–3	Water	5–8	8–12
FFA	6–10	5–7			

Table 4.9 Commercial Syndet Raw Materials and Ready-to-Use Bases

Company Name	Base Material Trade Name	Base Material Type
Ajinomoto Inc.	Amisoft CS-11	Sodium cocoyl glutamate
	Amisoft LS-11	Sodium lauroyl glutamate
Akzo Nobel	Elfan AT 84	SCI[a]
Bradford	Jordapon SB II Syndet Base	SCI + SS
Innospec	Tauranol I-78-C	SCI
	Tauranol I-85-T	SCI
	Syndet Base 96-143-1	SCI
Hampshire Chemical Corp.	Hamposyl	Acyl sarcosinate
Clariant	Hostapon SCI 65	SCI
	Hostapon SCI 85	SCI
Galaxy	SN 8212	SCS + DSLSS
	SN 8501D	SCS + SPLS + DSLSSb + SCG
	SN 8102	SCS + SPLS + Soap
Rhodia	Geropon AS-200	SCI
	Geropon SDT	SCI + Soap
Tensa Chem	Tensianol N1LM/N1A	SPCS
	Tensianol 815/815C	SPLS + DSLSS
	Tensianol SF/ISL/STM/DEO	SPLS + SCI
	Tensianol 3456 B/3720/ 3713 /3714/400	SCI + DSLSS
Zschimmer and Schwarz	Zetesap 813A	DSLSS + SCS
	Zetesap 5165	DSLSS + SCI
	Zetesap 5213	DSLSS + SCA
	Zetesap ST 5251	DSLSS + SCS + SLES

[a] SCI raw materials contain free fatty acids (stearic and coconut) in proportions of 5–10% for 85% SCI and 20–30% for 65% SCI, and free sodium isethionate of 2–4%.

[b] SLS and DSLSS are currently supplied as commodities at 30–95%.

Abbreviations: Sodium/potassium lauryl sulfate (SPLS); sodium/potassium coco sulfate (SPCS); sodium coco sulfate (SCS); sodium cocoyl isethionate (SCI); disodium lauryl sulfosuccinate (DSLSS); sodium lauryl sulfoacetate (SCA); sodium lauroyl sarcosinate (SS); sodium cocoyl glycinate (SCG); alkyl glyceryl (ether) sulfonate (AGS); sodium lauryl ether sulfate (SLES), and sodium lauryl sulfate (SLS).

salt, and 2% of superfatting agents. Ready-to-use Zest flakes of similar formulation were also offered (Procter & Gamble, 2000, 2001, 2003).

Ready-to-use combo flakes were launched by Galaxy under the name "SN 8102." One can use this base as such or dry mixed, properly mixed with soap flakes in various proportions, from 80:20 to 20:80 (Galaxy Surfactants, 2008).

Valuable support is given by most raw-material suppliers in providing suggested formulations for optimal performance, and by the syndet- and combo-based noodles (pellets/flakes) to overcome processing problems. TensaChem offers probably the broadest range of syndet bases, defined as "fully formulated soap-free flakes for cleansing-bar manufacture" (TensaChem, 2006) (Table 4.9).

Clariant has done extensive development work to promote Hostapon SCI use in combo and syndet bars (Clariant, 2003). The "grittiness," a characteristic problem of SCI bars, was researched, and relevant parameters to be mastered were considered. This crystallization phenomenon, which sometimes occurs under storage, was influenced by the way the soap is made. Higher mixing temperature, longer and more intensive mixing, fluid (water, etc.) presence, and additional milling were recommended.

The crystal-size distribution of the SCI material is also an important factor mastered by the supplier. As recommended, one should make a grittiness assessment immediately and at 4 weeks and 3 months after production (Clariant, 2003). Due to the high mixing temperature (100–150 °C) and the high moisture level (10–18%), SCI is susceptible to hydrolysis. The electrolyte level had some effect on limiting the amount of SCI lost through hydrolysis (Clariant, 2003; Unilever, 2000).

Zschimmer and Schwarz (2007a, 2007b) expanded its range of syndet compounds by launching Zetesap ST 5251, recommended for a variety of formulations. The solid emulsion system and the resulting liquid-crystal structures of the syndet base, combined with the advanced formulation, are considered to give the ideal base with a smooth touch and an exceptionally creamy foam.

Therefore, the consumer perception will evaluate dense creamy foam as superior to bubbly foam, ranking it as a more caring washing product.

Cleansing Efficiency

An interesting evaluation of the cleansing effect of various bars indicates that alkyl sulfate/sulfosuccinate blends have higher cleansing power, when compared to acyl glutamate and triethanolamine soaps, as presented in Figure 4.7 (Weber, 1987). The acyl isethionates were not tested for in Weber (1987). The cleaning activity was determined with a skin-washing machine that cleans the artificially stained skin of the forearm under standard conditions (Molls & Schrader, 1984).

By another proposed evaluation method, a fat-based ointment that simulated dirt, was placed on the dorsum of the hand and washed in a rotating soap solution for 5 min-

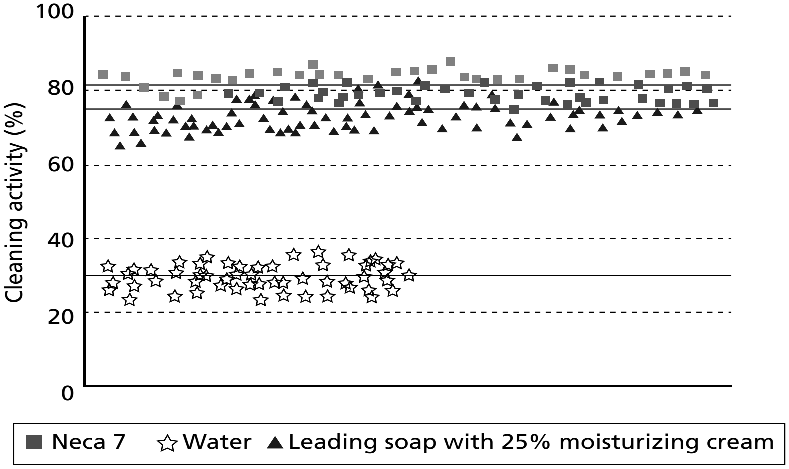


Figure 4.7 Skin cleansing efficiency of two different cleansing products compared to water.
Wolf & Friedman, 1996.

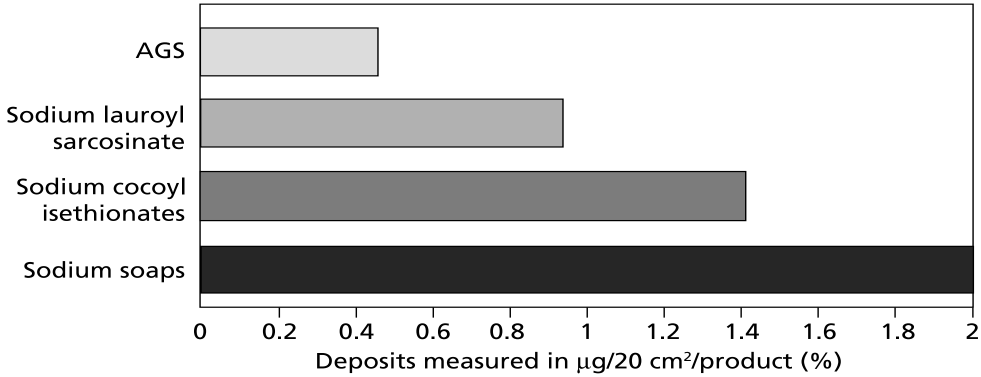


Figure 4.8 Rinsing efficiency and depostion profile of different surfactants.

utes. The cleansing efficiency of various soaps was assessed by comparing sebumeter reading before and after the washing (Wolf & Friedman, 1996). Better results, as shown in Figure 4.7, have been found for alkyl sulfate–based bar soap compared to leading isethionate brand, specifically 81% versus 75% cleansing capacity; water gave about 30%. Deposition profiles checked in P&G patents and unpublished/commercial publications (*New York Times,* 2001; Unilever, 2002) also evaluate rinsing/cleansing efficiency.

AGS was found to rinse cleaner and deposit less compared to SCI, while sodium soaps were found to have a much poorer cleaning efficiency (Procter & Gamble, 2000, 2001, 2003). This data emphasizes again the high surfactant tolerance to hard water given by the higher solubility of magnesium AGS and calcium AGS compared to sodium AGS; this results in AGS that rinses cleaner and deposits less. The rinsing efficiency and deposition profile of several surfactants is shown in Figure 4.8 (Procter & Gamble, 2000, 2001, 2003).

Foaming/Lathering

The foaming properties of different surfactants and finished syndet formulations can be checked by several methods whose descriptions are beyond the scope of this chapter. A common and reliable test to check foam volume and height is the mechanical inversion test. When checked in hard water (320 ppm $CaCO_3$), a higher foam performance was found for alkyl sulfate and sulfosuccinate formulations compared to isethionate-based syndet/combo bars and natural soap (Friedman & Wolf, 1996) (Figure 4.9). However, this test doesn't give any information on the foam quality, as a more bubbly foam gives more volume than a dense creamy foam, the latter being better appreciated for moisturizing formulations. Therefore, the consumer perception will evaluate dense creamy foam as superior to bubbly foam, and taking as a more caring washing product. Even the classic Ross-Miles method (Ross & Miles, 1953) is still being used in recent patents (Massaro et al., 1995); for instance, an initial foam height of 153 mm, collapsing to 5 mm after 10 minutes was found for C12 lactobionamide compared to an initial height of 145 mm that stays stable at 140 mm after 10 minutes for C14 lactobionamide. It is evident that the sensitivity of foam stability measurements depends on the hydrophobic chain.

Expert-rated panel-lathering tests are seldom preferred (Gattir & Matthaei, 1975), reporting especially on speed of formation, quality of foam, and lather feel during washing.

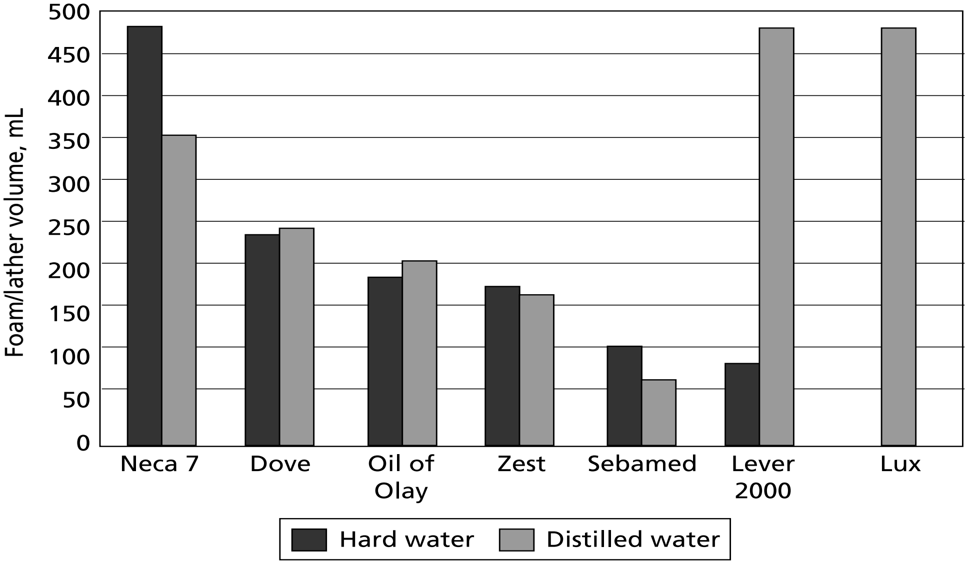


Figure 4.9 Foam/lather performance. Water hardness, 320 ppm $CaCO_3$; water temperature, 30 °C; product concentration, 0.16 wt %.

Lather volume is also practically determined by accumulating the lather generated by rotating a bar 10 times with a wetted glove under a stream of water at a given temperature (Massaro et al., 1995). Some results from the German DIN 53902 method are reported for ethoxylated isostearyl monoglyceride added to the syndet solution; they reduced foam from 500 mm to 150 mm (Hollstein & Spitz, 1982). Hydrophobic additives, selected for their emollient or plasticizing contribution, reduce foam considerably.

To enhance the lather performance of the primary surfactant in lather formation speed, stability, or cold water performance, some foam enhancers can be used. Dodecyl benzene sulfonate, sodium lauryl sulfate, alkanolamides, and even neutralized fatty acids perform this function well. Alkyl polyglucosides (APG) have been promoted recently by Cognis (2001) and Seppic (2001) as foam enhancers, especially in soap formulations containing 1.2–1.5% Plantaren/Plantacare (Cognis, 2001) or Oramix (Seppic, 2001). Both companies suggest that the same result was perceivable in syndet/combo formulations. Cognis reports on SCI:soap combo (ratios 50:8 to 70:8 on 100% active basis) with 8–9% APG showing improved processability and lathering as compared to the non-APG original base; 15% APG is also recommended as a co-surfactant in a syndet based on 40% DSLSS and 15% paraffin wax as a lipid-layer enhancer.

Plasticizers and Binders

To obtain good processability and usage properties, the formulation is stabilized with plasticizers and binders. Plasticizers are included to facilitate better extrusion and stamping of the syndet bar. The plasticizers act by lowering the viscosity of the material at the manufacturing temperature, providing flow under pressure.

Binders prevent separation of macroscopic aggregates, caused by local stress, and provide cohesion and anticracking behavior of the solid product. Natural soap does not have plasticity problems, as the soap itself is a classic plasticizer, beyond its cleansing surfactant role. Plasticizers and binders strongly influence lathering, mushing, and wear characteristics. Generally, the plasticizers and binders are used together, and one material can perform at least two roles. They are able to absorb some or all of the free water of the syndet, bind the various ingredients together, plasticize the mass, and act as emollient simultaneously. The plasticizers most commonly used are long-chain fatty alcohols (higher than C16), polyol esters (glycerol monostearate, sorbitan stearate, and glycerol mono- and distearate), polyethylene glycol, sodium stearate, stearic acid, fatty acid ethoxylate, hydrogenated castor oil, paraffin wax, fatty alkyl ketones, and a combination of hydrogenated triglycerides with fatty alcohols or acids (Hollstein & Spitz, 1982; Friedman & Wolf, 1996).

As pointed out in Table 4.7 (Beerse et al., 1995), at least 20% plasticizers are used; these are comprised of fatty acids and paraffins that are solid at room temperature but are malleable at bar-plodding process temperatures of about 35–45 °C. The binder used in the same patent is any material that is by itself liquid, and is selected from water, liquid polyols, and even fragrance. Their levels in the bar are theoretically 3–20% water and 0–15% polyols (Beerse et al., 1995).

The plasticizers and binders have high melting points and high olecular weights. It seems that their binding activity is obtained when the melting point of the mass is simply raised. Ingredients, such as gums and gum resins, provide additional cohesion by acting as binders.

Some patents (Fair & Farrell, 1995) describe the binder as stucturer, specifically referring to polyalkylene glycol (25–60%). Recent patents (Kacher et al., 1993a, 1993b, 1993c) define special binding as formation of a rigid crystalline phase skeleton structure, comprising an interlocking, open, three-dimensional mesh of elongated crystals. The crystals in this case, essentially consist of 5–50% (Kacher et al., 1993a, 1993c) or 10–50% fatty acids, of which 20–65% are neutralized, in addition to 15–65% (Kacher et al., 1993c) or 20–65% (Kacher et al., 1993a, 1993b) of anionic and/or nonionic bar firmness aid, including a relatively high water content of 15–55% (Kacher et al., 1993b) or 15–40% (Kacher et al., 1993a, 1993c). The surprising aspect of this invention is that bar hardness and low smear are obtained in the presence of soft hydrophobic materials (including petrolatum, paraffins, and most natural and synthetic waxes), nonionic solvents/co-solvents (propylene glycol, glycerine, etc.), and anionic surfactants that typically result in bar softening. This results in the interlocking crystalline skeleton network that contains substantial "void" areas being filled by soft and/or liquid aqueous phases; this drastically changes the colloidal structure and, consequently, the physical properties of a conventional bar. The only disadvantage of this almost ideal bar is that it is not extrudable under normal working conditions, and its preparation is made by pouring the molten mixture into a bar-shaped mold (Kacher et al., 1993a, 1993b) or by a freezer process in which the molten mixture is cooled to a semisolid in a scraped wall heat exchanger and then extruded as a soft plug, cooled and crystallized, and fed on a moving belt (Kacher et al., 1993c). Worth mentioning are several patents (Moran, et al., 1993; Constantine, 1989) proposing solid shampoo formulations that are processed in a molded form, basically formulated with alkyl sulfates.

Cast (Poured) Transparent/Translucent Syndet/Combo Cleansing Bars

The ultimate challenge of the syndet/combo market is to create an extrudable transparent/translucent of a neutral pH. Technically this target has not yet been achieved, but in the meantime the market segment of cast (also called poured, molded) transparent combo bars is steadily increasing. Beside the concept of purity and aesthetic appeal, this target provides a way to produce milder formulations with enhanced skin properties. With regular extrusion techniques, both soap and syndet bars have limitations to the amount of additives that can be used. These limitations can be overcome by using the cast-pouring techniques, while maintaining only a minimum degree of stickiness and mushiness. The special bar binding through formation of a crystalline skeleton network (Kacher et al., 1993a, 1993b, 1993c) seems to give the required bar hardness and low smear for a pourable transparent combo bar containing SLS, SLES, SCI, and CAB (cocamidopropylbetaine) together with fatty acids, PEG, paraffin wax, and silicones (Whalley, 2000).

Several commercial combo bases are offered on the market by different suppliers, such as Stephenson, Galaxy, TensaChem, and Unichema. Crystal ST from Stephenson is a hot-pour base containing sodium stearate/stearic acid, sodium laurate/lauric acid, and SLS/SLES surfactant mixture besides a glycerine/propylene glycol/sorbitol clear matrix (Stephenson, 2003). The Galaxy SN-900 series used in transparent combo body wash bars contain 25–40% soap, 25–35% glycols, 10–15% anionics (SLES) and amphoterics (CAB), 10–15% sugars, and 10–15% moisture (Galaxy Surfactants, 2003). A recent patent (Jaworski & Park, 2002) claims a transparent bar using a synthetic detergent and a soap having an enhanced transparency, clarity, and mildness not achieved previously. The composition is: 40–45% surfactant (of which 15–35% is an SLES type); 10–30% of a polyhydric alcohol (such as propylene glycol, glycerol, sorbitol, or PEG); 15–30% soap; and 5–20% alkanolamide as a foam stabilizer. A preferred pH of 9.6 and not below 8.0 (because of loss of clarity and hardness) is claimed. Surprisingly, the claimed product has mildness equal to Dove as checked by a modified soap chamber test, even at this relatively high pH (Frosch & Kligman, 1979; Jaworski & Park, 2002).

Transparent and translucent combo bar formulations have been commercially promoted by adding nonoxynol-10-carboxylic acid and C12–15 alkyl benzoate to the soapsyndet base (Finetex & Novakovic, 1989). Commercial offerings of cleansing bars based on sarcosinates (Hampshire, 1994) or acyl glutamates (even of translucent appearance) (Ajinomoto, 1994) have been made during the last few years, in spite of the industrially inefficient hot-pour manufacturing method used. A beautiful, round-shaped acyl glutamate syndet has recently been launched by Ajinomoto in a Korean–Japanese venture that is being promoted abroad (Ajinomoto, 2001). This is a so-called gel soap called Amino Crystal, emphasizing the main amino surfactant, TEA cocoyl glutamate; additional components are decyl glucoside, hydrolyzed collagen, dipotassium glycyrrhizinate, glycerine, urea, and isopropyl alcohol.

Performance- and Appearance-Improving Additives

One perceptible drawback of the syndets is their solubility and mushiness in water, which is known as *bar smear* or *bar slough.* This messy, unattractive, and uneconomical property is due to the high solubility of some surfactants and inappropriate formulation. Under certain formulations, this paste-like mush is unable to return to a solid state by losing water from the mush layer. Using higher water levels in the formulation will result in the wanted manageable neat phase (also known as the G or lamellar phase) transforming into a viscous jelly-like middle phase. One major solution used for alkyl sulfate syndets is to use their potassium salts, which gives a low mushiness and an economical base.

Other low-solubility enhancers are inorganic salts, such as sodium sulfate and sodium chloride. A recently patented process produces a soap and combo bar with 0.5–10% auxiliary mild surfactants (Aronson et al., 2001); these bars have enhanced skin-care properties from the addition of protic acid salts (PAS) to soap formulations with fatty acid soaps, free fatty acids (FFA), and polyalkylene glycols. A protic acid is any acid that readily yields protons, for example, a Brønsted acid. The salts of such protic acids are selected from inorganic and organic acids, with preference being given to sodium chloride/sodium sulfate for the inorganic, and sodium lactate/sodium citrate for the organic. The required ratio FFA:PAS of 0.5:1 to 3:1 is highly emphasized (Aronson et al., 2001).

Aluminum triformate efficiently reduces water solubility in sulfosuccinate formulations (Hollstein & Spitz, 1982). Slipping has been obtained by adding zinc stearate (recently reappearing in the ingredient list of Extra Sensitive Dove brand, marketed in Europe) and ethoxylated sorbitan ester (Milwidsky, 1985; Hollstein & Spitz, 1982). Preferred slipping agents are high molecular weight ethylene oxide polymers (such as PEG 14M) (Aronson et al., 2001). Sodium isethionate is added in acyl isethionate formulations to reduce wear rate (Tokosh & Cahn, 1979).

Bar appearance (water retention and/or shrinkage prevention) aids are seldom selected from a long list of water-soluble organics, salts, clays, and suitable waxes (preferably paraffin) to impart skin mildness, plasticity, firmness, processability, glossy look, and smooth feel to the bar (Kacher et al., 1993a, 1993b, 1993c). Antibacterial additives, such as trichlorocarbanilide and triclosan, are good examples of successful additives for deodorant and antibacterial bars, even if their use is currently being questioned.

Fillers

The fillers are, by definition, cheaper ingredients, used to reduce the bar cost. In the case of syndets, the fillers are not inert ingredients but participate in improving the internal structure and hardness of the finished product. Fillers can therefore be called additional binders. The best-known fillers are dextrin, starch, and modified starch (degraded, ethoxylated).

Talcum powder has also been used as a filler to aid against mushiness, while buffered borax is added to reduce specific gravity and lower wear. The drawbacks of the fillers are a rough surface texture, loss of slip, and loss of attractive overall appearance. For this reason, one should not exceed an optimal concentration of these substances. Recently, Luzenac (2002) promoted new talc grades presented as innovative technology and applications for soaps and syndets (Luzenac, 2002; Arseguel, 2003).

The list of fillers quoted by Hollstein and Spitz (1982) also notes sodium sulfate, $CaHPO_4$, $MgHPO_4$, NaH_2PO_4, dextrin, and mannitol as being state-of-the art examples. A current state-of-the-art list will include calcium carbonate and talcum (1–40%), aluminosilicate clays and/or other clays (0.5–25%), and salt and salt hydrates (1–40%) of almost any existing cations and anions (Kacher et al., 1993a, 1993b, 1993c). Sometimes wheat flour is preferred to cornstarch since it imparts a more acceptable wear rate to an acyl isethionate bar, which can contain between 25% to 65% filler (O'Roark, 1966).

Mildness Improvers/Skin Conditioners/Moisturizers

The formulation of a mild or even ultra mild soap–syndet has become a top focus in the field; a great deal of research and development was devoted to make soaps milder. Moisturizers, emollients, and superfatting additives were included to provide skin conditioning benefits and to improve mildness. Most of them are presented in Table 4.10 (Medcalf et al., 1987; Mausner, 1981). The "superfatting" term comes from fats and oils found in the

Table 4.10 Moisturizers/Emollients in Soap–Syndet (Combo) Bars

Moisturizer	Purpose	Type of Raw Maeterial
Occlusive	Deposit on skin surface, reducing rate of evaporation	Long-chain fatty acids (25% moisture cream), mineral oil, ethoxylated/propoxylated ethers of lanolin alchol or methyl glucose, vegetable oils.
Non-occlusive	Hygroscopic substances to stratum corneum, retaining water, improving lubricity	Glycerine, proplylene glycol, polyols, sorbitol, lactic acid, pyrolydone, carboxylic acid, urea, L-proline, guanidine, pyrolydone, hexadecyl, myristyl, isodecyl, isoprorpyl esters of adipic, lactic, oleic, stearic, isostearic, myristic, or linoleic acids, isotearyl 2-lactylate, sodium capryl lactate, proteins, aloe vera gel, acetamide mea.

soap boil in excess of stoichiometric needs. As in conventional soaps, the superfatting additives promote in the syndet/combo bars a denser, creamier lather, that leaves the skin smoother and softer. Classical superfatting agents that were used in alkali soaps, such as palm and olive oil (Palmolive), cocoa butter (Tone), and fatty acids (Coast/Shield), are also of practical use in syndet/combos (Piso & Winder, 1990). The addition of these additives has a plasticizing effect on the base, so that moisture content usually needs to be lowered and the hardening agent content (such as salt) has to be increased.

Patented skin conditioning/mildness aid agents seldom listed are hydrated cationic polymers selected from a broad range of cationic polysaccharides, cationic, co-polymers of saccharides, and synthetic cationic monomers of synthetic nitrogen polymers (Massaro et al., 1995; Pichardo & Kaleta, 1993). A preferred polymer is a hydrated cationic guar gum having a molecular weight range of 2,500–350,000. Incorporating 1% cationic guar gum (such as Jaguar C-14-S) to soap/syndet (about 67% soap) formulation is reported to reduce the erythema/dryness score below that of a Dove-type formulation, when checked by in vivo forearm test (Massaro et al., 1995). A new version of Dove, launched in 1995, unscented and recommended for sensitive skin, contains cocamidopropyl betaine that was seldom included in European formulations for its synergistic improvement of anionic surfactant mildness. Since then, betaine became the preferred foaming mild co-surfactant and replaced the harsher DDBS in all the new versions of Dove.

Some 2-in-1 soap and cream concepts have been solved not by soapless formulations but by including skin mildness and moisturizing additives with mild surfactants. Examples are FA 2-in-1 Soap and Cream with sodium myreth sulfate, decyl glucoside, sodium laureth sulfate, sodium lactate; Monsavon 2-in-1, Savon et Creme with 25% base hydratante, containing ceteareth 80, glycerine, guar hydroxypropyl trimonium chloride; and Palmolive 2-in-1 Wash & Creme with disodium lauryl sulfosuccinate, coconut acid, stearic acid, and lanolin.

A comprehensive ingredient list of the most well-known syndet and combo bars is given in Table 4.11. The ingredient lists for most formulations have been updated to the 2003 formulation list. Table 4.11 demonstrates the dynamic nature that formulas must possess to be able to cope with the market, consumer, environmental, and regulatory changes, while providing formulation improvements.

Striking differences are sometimes found for the same multinational brand manufactured in different parts of the world. For instance, U.S. Zest is based on sodium glyceryl ether sulfonate (SGCS), while Zest Mexico contains potassium lauryl sulfate instead (Table 4.11).

Table 4.11 Syndet/Combar Compositions (from Ingredient Labels)

Vel[a]	**Dove Exfoliating[b]**	**Dove Nutrium[b]**	**Caress[b]**	**Dove[b]**
SCI; Stearic acid; Sodium tallowate; Water; Coconut acid; Sodium isethionate; SC/SPK; HCO; Fragrance; Titanium dioxide; Glycerine; Sodium chloride; PSP	SCI; Stearic acid; Sodium tallowate; Coconut acid; Water; Sodium stearate; CAB; SC/SPK; Fragrance; Sunflower seed oil; Tocopheryl acetate; Sodium chloride; Polyethylene; Tetrasodium EDTA; TSE; Titanium dioxide	SCI; Stearic acid; Sodium tallowate; Water; Sodium isethionate; Coconut acid; Sodium stearate; CAB; Sunflower seed oil; SC/SPK; Fragrance; Lanolin alcohol; Tocopheryl acetate; Glycerine; Sodium chloride; Titanium dioxide; Tetrasodium EDTA	SCI; Stearic acid; Coconut acid; Sodium tallowate; Water; Sodium isethionate; Glycine soja oil; Sodium stearate; CAB; Mica; SC/SPK; Fragrance; Sodium chloride; Tetrasodium EDTA; TSE; BHT; Titanium dioxide	SCI; Stearic acid; Sodium tallowate; Water; Sodium isethionate; Coconut acid; Sodium stearate; CAB; Parfum; SPK; Sodium chloride; Trisodium EDTA; Zinc stearate; TSE
Cataphil[c]	**Zest Mexico[d]**	**Zest[d]**	**Lever 2000[b]**	**Olay[d]**
SCI; Stearic acid; Sodium tallowate; Water; Sodium stearate; DDBS; Sodium cocoate; PEG-20; Sodium chloride; Fragrance; Sodium isethionate; Peterolatum; SIL; Sucrose laurate; Titanium dioxide; PSP; TSE	Sodium tallowate; Magnesium tallowate; PLS; Sodium cocoate; Water; Talc; Sodium sulfate; SLES; Magnesium cocoate; Fragrance; Sodium chloride; Titanium dioxide; Citric acid; Sodium citrate; PSP	Sodium tallowate; SCGS; SC/SPK; Magnesium cocoate; Water; Magnesium tallowate; Talc; Sodium chloride; Tricolocarbon; CP/PKA; Fragrance; Titanium dioxide; Tallow acid; PSP; TSE	Sodium tallowate; SCI; Sodium cocoate/laureate; Water; Sodium isethionate; Stearic acid; Coconut/lauric acid; Fragrance; Sunflower seed oil; Tocopheryl acetate; WGAPD; Hydrolized wheat protein; Titanium dioxide; Sodium chloride; Disodium phosphate; Tetrasodium EDTA; TSE; BHT	SCI; Paraffin; SCGS; Glycerine; Water; Magnesium silicate; Magnesium stearate; Sodium isethionate; Stearic acid; Magnesium cocoate; Coconut acid; Sodium stearate; Sodium cocoate; Fragrance; Magnesium laurate; Titanium dioxide; Lauric acid; Sodium laurate; Tetrasodium EDTA; TSE; PEG-90M
Eubose	**Satina**	**Lanosan**	**Nivea Milk Bars**	**Sebamed**
DSLSS; Sodium coco-sulfate; *Triticum vulgare;* Cetaeryl alcohol; Paraffin; CAB; PEG0CCG; Water; Glycerine; Allantoin; Aluminum formate; Titanium dioxide	SCI; Glyceryl distearate; PEG-200; Cornstarch; Paraffin; DSLSS; Coceth 20; Petrolatum; Panthenol; HAP; Basbolol; Disodium EDTA; Sodium hyroxide; Fragrance	Paraffin; SCI; DSLSS; Glyceryl stearate; Sucrose; Water; Lauryl polyglucose; Milk protein; CAB; Citric acid; Stearic acid; Aluminum triformate; PEG-GI; Betraine; PEG-45M; Ceteary alcohol; Fragrance	SCI; Stearic acid; Sodium tallowate; DSLSS; Sodium cocoate; Coconut acid; Paraffin; PEG-150; Parfum; Sodium chloride; Tetrasodium EDTA; Sodium etidronate; Glycerine; Lanolin alcohol	DSLSS; *Triticum vulgare;* Paraffin; SCI; Glyceryl stearate; Stearic acid; Palmitic acid; Cetyl palmitate; Cetyl palmitate; Cetaryl alchool; Water; Lecithin; Sodium lactate; Tocohperyl acetate; Glycine; Magnesium aspartate; Mixture (M[i]); Parfum

[a]Colgate-Palmolive; [b]Unilever; [c]Bayer; [d]Procter & Gamble; [e]Dr. Holgein; [f]Wella; [g]Beiersdorf; [h]Sebapharma; [i]Alanine pyroxidone HCl, lysine, leucine, urea phosphate, polyquarternium 22, disodium EDTA, PEG14 M.

Abbreviations: Cocoamidopropyl betain (CAB); Coconut/palm kernel fatty acid (CA/PKA); Disodium lauryl sulfosuccinate (DSLSS); Hydrolyzed animal protein (HAP); Hydrogenated casor oil (HCO); PEG-6 Caprylic capric glycerides (PEG-CCG); PEG 15 Glyceryl isostearate (PEG-GI); Pentasodium pentetate (PSP); Potassium lauryl sulfate (PLS): Sodium cocoate/sodium palm kernalte, SC/SPK; Sodium cocoyl iesthionate, SCI: Sodium cocoglyceryl ether sulfonate, SCGS; Sodium dodecylbenzene fulfonate, DDBS; Sodium isosteraoyl lactylate, SIL; Sodium laureth sulfate (SLES); Sodium palm kernlate (SPK); Trisodium etidornate (TSE); Wheat germ amidopropyl demithylamine (WGAPD).

Design of the Dove Beauty Bar—A Development Showcase

An interesting paper on the experimental approach used in the development of the Dove Beauty Bar was recently presented by Hill and Post (2005). Defining the original product-design problem as the formulation of "a non-soap cleansing bar that did not leave a bathtub ring," the paper emphasizes, besides this primary attribute, several secondary properties essential for a successful product. These additional properties relate to consumer perception of firmness, rich and creamy lather, absence of grit, skin mildness, absence of unpleasant odors or colors, slippery-wet feel, low mush rate, and no cracking. Processing attributes are also included.

The logics of the product-design problem followed by the problem- solution strategy offer to the reader a prototype of good research and development practice. The presentation provides detailed data of the Direct Esterification of Fatty Acid and Sodium Isethionate (DEFI) process, used commercially by Lever Brothers Co. (Cahn et al., 1967), and Unilever screening tests for lather (Farrell & Nunn, 2005), odor stability, color, wet feel, mush (Van Gunst et al., 2001), firmness (Haass & Lamberti, 1968), and processibility (Post et al., 1997).

Product formulations affect the listed final-product properties:

- Higher lather by pH adjustment and co-surfactant choice (DDBS preferred)
- Higher stability of odor and color by appropriate choice of partially hydrogenated coconut fatty acid (to 3–5 IV) as preferred raw material for SCI
- Better binding and plasticity and lower cracking by using a combination of long-chain fatty acid (25–30 %) and sodium soap (5–10%)
- Lower cracking, while assuring a lower water absorption by keeping the pH not appreciably above 7
- Better extrusion and stamping by keeping water content at about 4–6%

All of the above make the paper an explicit formulation showcase, revealing a deep understanding of the ingredients–performance relationship. In this respect, it is similar to previously presented patents (Beerse et al., 1995). The original solutions of the product-design problems, as proposed 30–40 years ago, stood the test of time of the most successful syndet bar on the market ever; Dove's composition has remained largely unchanged to this day (Hill & Post, 2005).

Mildness Concept

Over the past 25 years, many changes in the approach to soaps have occurred. The turning point was in 1979 when Frosch and Kligman (1979) described a new method to assess soap irritant properties. They demonstrated that the chief weakness of the existing tests was that under normal usage conditions, the reactions were weak and did not discriminate between different soaps. They proposed the soap chamber test (SCT) to conduct tests on people known to have sensitive skin under extreme conditions, thus producing strong reactions that emphasize the differences between various soaps (Frosch & Kligman, 1979). After five weekday Duhring chamber exposures to 8% soap solutions (24 hour application in the first day, 6 hour applications in subsequent days), the skin reactions (erythema, scaling, and fissures) are read and rated. A soap is characterized as mild and non-irritant when the total score is less than 1 and harsh when it is close to 5, the maximum score.

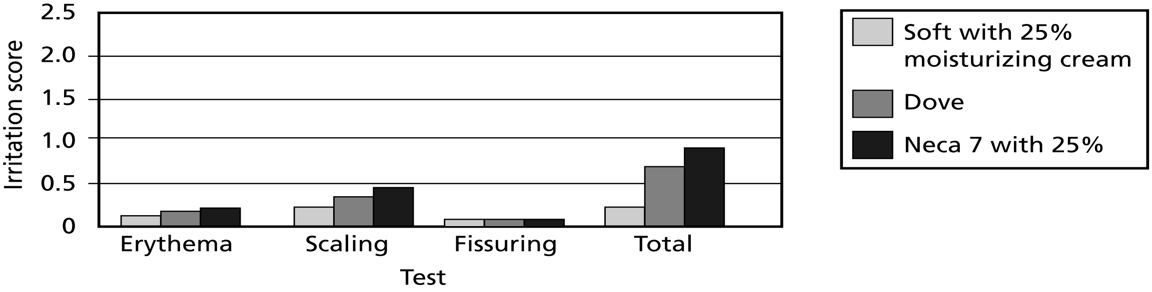


Figure 4.10 Soap chamber test of 0.06 mL (8% w/v), overall mean score.

Tests performed in Israel in 1992 confirmed Dove mildness, producing similar results for Neca 7 syndet with 25% moisturizing cream and Soft with 25% moisturizing cream (Figure 4.10). The two local brands were based on SCI/DSLSS soap-free syndet blends. However, similar tests made in the UK during the winter of 1993 scored Lever 2000, considered to be mild, around 2.0, while Neca 7 and Soft scored 0.9 and 1.6, respectively (Internal Neca Publication, unpublished). The total overall mean score was primarily due to the erythema results, while the scaling and fissuring values were lower than 0.2 for all the products.

Climate conditions and skin panel sensitivity greatly influence the results, as already found and reported by Frosch and Kligman (1979). Similar large variations in the SCT mildness scores for Dove over the course of a year have been reported, showing values from 1.05 to as high as 2.65 (Aronson et al., 2001). Thus, whenever certain bars were evaluated, the mildness of both Dove and Ivory (used as a control for a so-called "irritant" product) were also evaluated (Aronson et al., 2001).

The lack of correlation that sometimes exists between consumer tester reports and the proposed Frosch and Kligman "toxicity ladder" is intriguing. Consumer survey reports from 500 women who took part in usage tests showed that the best-liked soap was Neutrogena Normal to Dry, which ranked first in all categories, including luxurious skin feel, quick rinsing, super cream feeling, and produced extra skin softness (Boughton & Huges, 1981; Wolf, 1994). Dove ranked much lower. The results contradicted the soap chamber test in which Dove was the leader and Neutrogena ranked seventh (Frosch & Kligman, 1979). Similar discrepancies between facial wash and SCT results have been reported by Frosch (1982). "The question then arises: What test actually reflects soap's quality most accurately—the irritancy tests under extreme conditions, or a broad survey of consumers? A not less important question is: What is the most important property of a soap—mildness, or cleansing power and feeling of the skin after use?" (Wolf, 1994).

A comprehensive survey of the models for surfactant–skin interactions that detail the mildness from in vivo and in vitro evaluation methods was compiled by Paye (1999) and is summarized in Table 4.12. As can be seen, the extreme usage conditions of SCT are obvious when compared to other in vivo tests that are normally used in state-of-theart patents and performed under realistic rinse-off usage conditions (application time not exceeding 90 seconds, compared to at least 6 hours in the SCT). For this reason, the SCT method has been largely replaced in the industry by other in vivo tests, such as the forearm-controlled application techniques. This methodology was also selected for a recent Unilever patent

Table 4.12 Mildness Evaluation Methods

Type of Test	Method	Reference
In vivo	Flex wash test (3 washes daily, total 15 washes) (60 sec. applications)	Redd et al., 1992; Medcalf et al., 1987
	Arm wash test (4 washes daily, total 40 washes) (90 sec. application) evaluate erythema, and dryness	Medcalf et al., 1987
	Forearm wash test (4 washes daily, total 17 washes)	Frosch et al., 1979
	Soap chamber (5 d, 24 h, and 6h × 4 applications) evaluate erythema, scaling, and fissures	Redd et al., 1992; Schwartz et al., 1991, 1992; Kacher et al., 1993a, 1993b; Wilsone et al., 1993; Frantz, 1975; Small et al., 1987
In vitro	*Skin barrier destruction test* Skin barrier destruction is measured by the relative amount of radio labeled water ($^3H–H_2O$) which passes from the test solution through a skin epidermis membrane into the physiological buffer contained in the diffusive chamber *Zein test* The Zein protein (similar to keratin) is solubilized in a surfactant solution. The Zein solubilized is determined by the released nitrogen content. The Zein number is measured as mg N/g surfactant. *Red blood cell (RBC) test* Hemoglobin denaturation of haemolysis test; measured by visual examination, transepidermial water loss (TEWL), or blood flow	Redd et al., 1992; Schwartz et al., 1991, 1992; Kacher et al., 1993a, 1993b; Wilson et al., 1993; Frantz 1995; Small et al., 1987

(Aronson et al., 2001) that used controlled application wash tests, such as the flex wash and arm wash tests to quantify the relative potential to induce irritation, skin barrier damage, and dryness. These tests utilize a combination of subjective evaluations (visual skin condition assessment by expert graders) as well as objective instrumental biophysical measurements to quantify the induced changes to the skin barrier function and the skin's ability to retain moisture (Aronson et al., 2001).

Mildness Evaluation Methods

Different protein denaturation in vitro tests have been developed to predict surfactant-induced eye or skin irritation (Paye, 1999). The Zein test is one of the widely used in vivo screening methods to evaluate local tolerance of surfactants (Table 4.12). Zein is a protein obtained from corn and resembles keratin. The Zein test developed by Gotte (1966) is based on the solubilization of the corn protein; the protein is normally insoluble in aqueous solutions unless denatured. It is incubated with the surfactant solution for 1 hour at constant temperature and under slight shaking. At the end of the incubation, the soluble fraction is separated from the insoluble one by centrifugation and filtration. As the surfactant-induced irritation increases, more Zein will be denatured and solubilized. Zein solubility in a surfactant solution is measured and given as mg nitrogen solubilized per gram of surfactant, known as the Zein Number (mg N/g). Values lower than 200 classify the product as mild and nonirritating. Zein values of different surfactants, as measured by Clariant (1999), are presented in Figure 4.11.

Combar mildness evaluation by the Zein test has been used in several patents, such as in a Unilever patent (Post et al., 1998). They found that a fatty acid soap containing 1–25% polyoxyethylene–polyoxypropylene surfactants (EO–PO polymer of ratio between 1.2:1 to 15:1 and a MW of 2,000–25,000) has enhanced mildness with no sacrifice in processability or lather. The claim was proved by showing that Zein values of combo bars containing about 34% soap, 14% SCI, 10% fatty acid, and 25% EO–PO polymers are lower by 40% when compared to non-EO–PO bars (Post et al., 1998).

The red blood cell (RBC) test also investigates the protein-denaturing effect of surfactants by using red blood cells as a biological material substrate (Pape et al., 1987). The surfactant solution causes hemolysis of the blood cells and subsequently releases hemoglobin into solution and partially denatures it. After eliminating intact cells and cell debris by centrifugation, the amount of released hemoglobin and the proportion of denatured hemoglobin are assayed spectrophotometrically. The capacity of the product to induce cell hemolysis is currently used to predict the eye irritation potential of the material, while the skin irritation potential is predicted from the proportion of pigment which is denatured (Paye, 1999). RBC values of different surfactants, based on Clariant results (Clariant, 1999; Henning et al., 1999), are presented in Figure 4.12.

Most of the P&G patents (Beerse et al., 1995) measure the surfactant mildness by a skin barrier destruction (SBD) test, developed by Franz (1975). One of the patent claims,

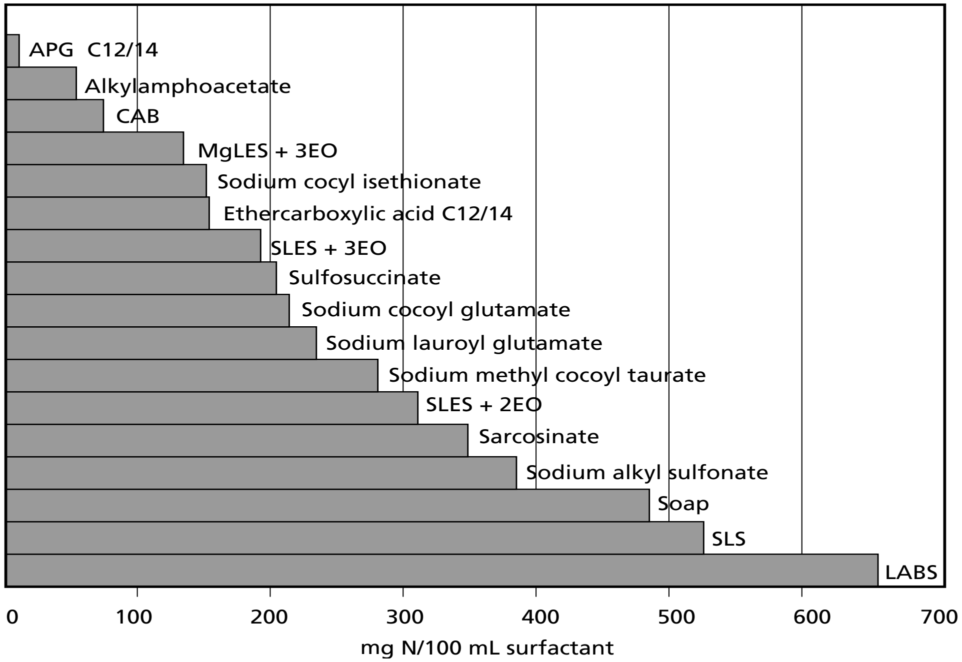


Figure 4.11 Zein values for various surfactants at 1% active matter.

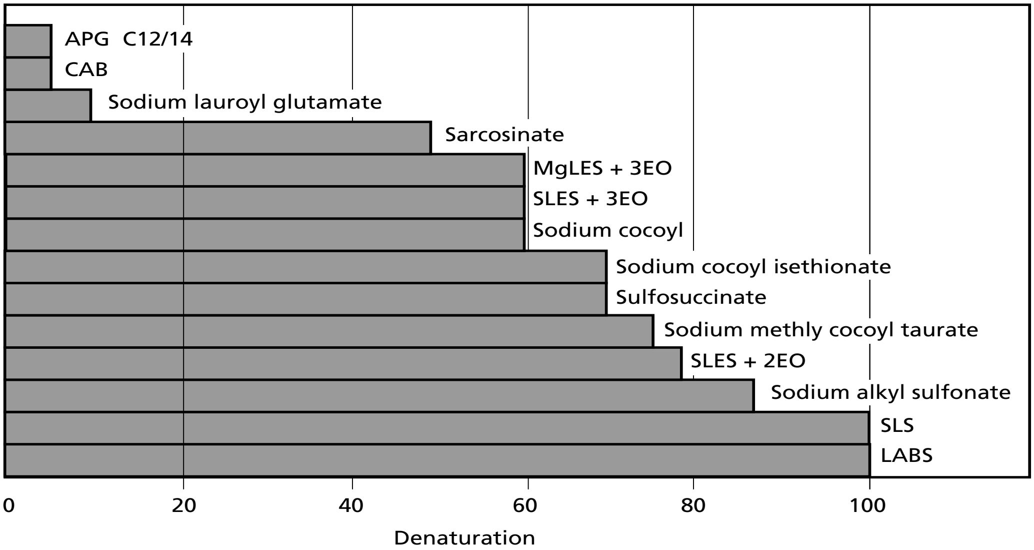


Figure 4.12 RBC values of different surfactants at 1% active matter.

based on SBD findings, is that the long-chain alkyl sulfates are milder than AGS and incorporation of 8–20% sodium cetearyl sulfate contributes to the required mildness of the specified product (Beerse et al., 1995). A surfactant mildness comparison, as measured by SBD test, has been also used by P&G to promote the newly commercialized AGS surfactant (Procter & Gamble, 2000, 2001, 2003). The results are presented in Figure 4.13. In Israel, one particular neutral soapless soap (Neca) commands about 30% of the market.

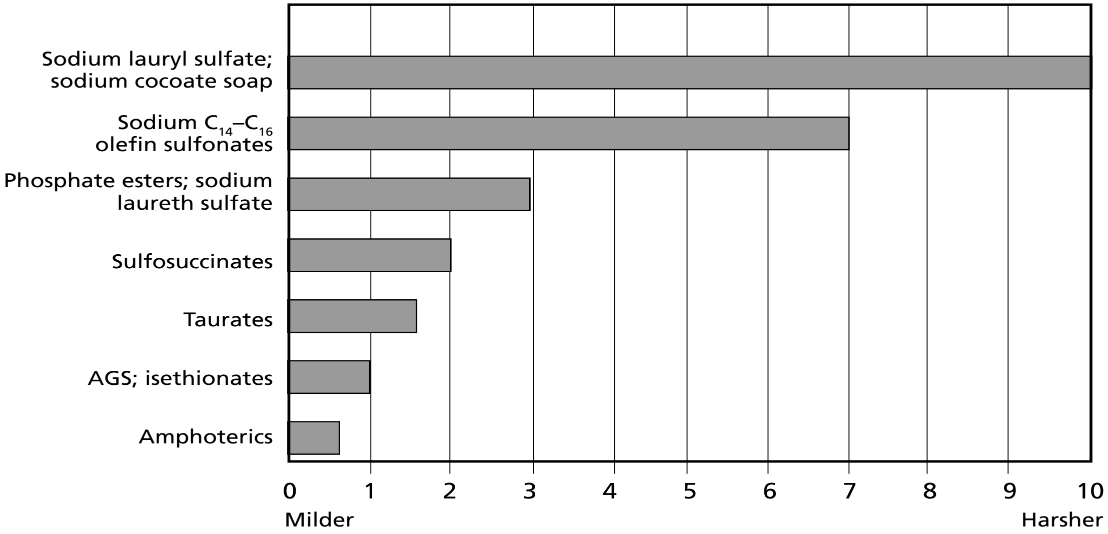


Figure 4.13 Surfactant mildness comparison.

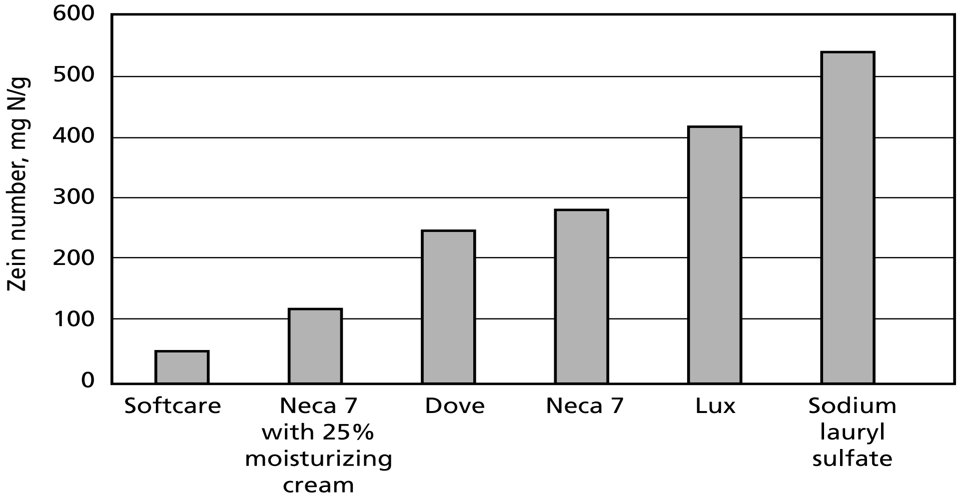


Figure 4.14 Zein number for various soaps.

Although it has been on the market for about 40 years and has undergone many clinical tests throughout that period, it has never lost its place as the most widely sold soap in the country. Testing this soap with the new methods produced confusing results. In SCT, Dove was shown to be much better than the local soap. In the Zein test, which generally correlates well with the results of the chamber test (Wolf, 1994; Kaestner & Frosch, 1981), the two soaps were equal; both were only moderately irritating (Figure 4.14). Another low pH soap, Softcare, has proven itself to be a very mild baby soap in clinical experiments in Israel. It was found to be much superior to Dove in the Zein test, 76 versus 272, respectively, and in the SCT the opposite was the case (Figure 4.14). The two local syndet brands are based on an alkyl sulfate/sulfosuccinate blends of different alkyl sulfate types and alkyl chain lengths as well as various AS/DSLSS ratios. The confusing results presented here raise the question of whether laboratory testing under extreme conditions is more reliable than clinical testing or consumer opinion that reflects decades of use. Should we rely on the sometimes confusing data that arise from very modern and sophisticated tests or on clinical tests and broad survey of consumers and usage tests (Wolf, 1994)? It seems that the answer can be found in the remark made by Frosch (1982) that “with regular use the soapless soaps . . . cause no adverse effects in people with normal skin . . . and are often beneficial to people of oily skins.”

“The wide acceptability of the mentioned soap is consistent with this remark of Frosch, since 80% of the population have oily to normal skin and therefore, laboratory testing under extreme and unphysiological conditions is irrelevant for them” (Wolf, 1994). This statement confirms later objective self-criticism of Kligman on the patch test procedure (Kligman, 1996). The proposed approach is a syndet bar “for each skin type” recommending soaps for normal to oily, normal to dry, and for dry and sensitive skin. Different formulations and ingredients should suit different skin types. For instance, an alkylsulfate/sulfosuccinate base is suited to normal to oily skin, while an isethionate base is suited to dry and sensitive skin.

Market Development

Syndet bars have come a long way since their first commercial development about 50 years ago. It was then that mild cleansing bars were formulated by German dermatologists for patients who suffered from "soap eczema" due to sensitive skin. At that time, the bar was composed of surfactants similar to those popular and still widely used in shampoos. In fact, some soapless soap manufacturers defined their bars as "solid shampoo," promoting a successful marketing approach. However, it is interesting to note that even today's patents (Orshitzer & Macander, 1977; Moran, et al., 1993; Constantine, 1989) recall this concept, but they refer to molded formulations. A similar approach was adopted by the Israeli market, the only one in which syndet cleansing bars cover over 50% of the total soap-bar market. This market share, favored by hard water considerations, is still greater than in any other market, although the current American and European markets have been growing tremendously.

At the beginning of the 1990s, Germany seemed to be the major European soapless soap cleansing bar market with 6% in soap volume but with 20% of the total value market, since syndet bars are much higher priced. The high price of the syndet bars was due not only to the more expensive formulation than the natural soaps, but was also due to the marketing positioning and strategy. Most of the successful brand names in Germany were positioned on a dermatological platform as premium-priced, upscale products; focusing on their skin benefits and selling primarily through pharmacies and drugstores resulted in a final consumer price of $2–3/100-gram bar. In France, where the soapless soaps are categorized as "pain dermatologique," leading brands account for about 2% of the total soap market and are priced similarly to their German counterparts.

Neca took an entirely different approach in Israel. Neca recognized the mass-market potential of a bar having the benefits of a synthetic soap but selling at a popular price. In 1964 the company introduced Neca 7, a soapless cleansing bar having a dermatological value similar to the European syndets but priced at $0.50–0.70/100-gram bar and marketed as an all-purpose cleansing bar.

Neca 7 quickly became the leading brand in Israel, and until now has commanded about 30% of the total soap market, surpassing the slightly lower market share of another local syndet bar, Hawaii, owned by Henkel. One can most likely consider Neca 7 and Hawaii the world's best-selling syndets per capita in the highest syndet market-share country in the world.

The same marketing approach was successfully applied in the United States by Lever Brothers, which followed the same strategy of mass-market distribution, pricing, and promotion for its soapless and combination cleansing bars (especially Dove and, more recently, Lever 2000). In 1955, Dove was introduced as being different from other toilet bars because it "looks like a soap, it's used like a soap, but it is not a soap." Later, Lever began emphasizing that Dove "contains one-quarter moisturizing cream" and "won't dry your skin like soap," which remains the slogan of the present advertising campaigns. After a 1979 successful dermatological promotion supported by Kligman tests reporting that Dove soap was the best for the skin, Dove's market share grew. In 1982, Dove began successful marketing to doctors; it increased its market share constantly until it surpassed 9% by volume in 1990, when unscented Dove was introduced, while the last original Dove patent expired (*New York Times,* 2001). By 1993, Dove was the best seller, accounting for 16.4% of the U.S. bar-soap market. The success of soapless and combo bars in the United States was so dramatic and sustained that in 1991 Lever Brothers was able to oust P&G from the leadership position in the toilet-soap market. Two years later, in 1993, P&G responded in this "soap war," and regained the leadership with the success of its Whitewater Zest and, especially, Oil of Olay cleansing bath bars. The marketing strategy of the Oil of Olay bar, "a beauty bar at a competitive price," helped P&G regain the top position by 1993.

The key to the P&G success was primarily due to over a decade of research and development that enabled the creation of a "unique formula, which contains a specially engineered synthetic cleansing system." This again emphasized the importance of a properly chosen formulation for a targeted cost-effective product. The 1999 Dove Nutrium skin-nourishing bar was launched, visually emphasizing a dual formula (white–pink strips) that contained natural skin needs. The white formula was advertised as a gentle cleanser, while the pink formula contained a nutrient-enriched lotion with vitamin E (*New York Times,* 2001). Dove advertising for 2002 emphasized "sensitive-skin innovations of unsurpassed mildness," comparing a relatively high erythema score (1.9) of a Cetaphil gentle-cleansing bar with a Dove Sensitive score that was only 1.4 (Unilever, 2002). The same advertising highlighted the proven compatibility for medicated applications containing Retin A and benzoyl peroxide (Unilever, 2002).

Dove Gentle Exfoliating Beauty bar was launched in 2003 and was formulated with small, soft, smooth blue beads that combined the brand's moisturizers with gentle exfoliation (Henson, 2003). During the last years, P&G was active too, focusing more on the emotional needs of consumers and launching a variety of new invigorating, fresh, and wild scents for Zest (Henson, 2003).

The continuous development of the combo bars in the United States gradually increased their market share. In 2002, the combo bars reached a market share of 48.3% out of a total bar-soap sales of 1/4 billion USD. Five of the 10 U.S. soap vendors of those days were combo bars (Dove, Lever 2000, Zest, Caress, Olay), with market shares of 23.7% (Dove) to 4.5% (Olay) (Euromonitor, 2002, 2003; IFF, 2002). Nevertheless, the data continued to show in 2002 an annual decrease of 3.8% in total bar sales, continuing to surrender to liquids. During the last years, bar-soap sales dropped further, and liquid-cleansing products increased significantly. The marketing titles of 2000, such as "liquids move up in the soap market," already emphasizing in 1999/2000 an annual increase of 7.7% in liquid-soap sales (Marchie, 2000), went on in 2002 when liquid soap rose 4.6% (Henson, 2002).

An overall view of the United States's and Western Europe's (big 5) markets of solid bars and liquid-soap alternatives (hand, shower, and bath) was compiled for 2001 from *Euromonitor* data (2001; IFF, 2002).

The European segment of all the personal-wash-products market includes the body washes, mainly in the bath-care segment; this probably also contains some more sophisticated cleansing items. However, the data show that overall, the alternative-cleansing sources—such as liquid soaps, shower gels, and body washes—outpaced the bars significantly. The bar-soap market share dropped to about 37% in the United States, 25.6% in the United Kingdom, 22.4% in Italy, 19.5% in France, 12.2% in Germany, and 11.1% in Spain (*Euromonitor,* 2001; IFF, 2002). For comparison, the *Euromonitor* statistics of the global soap market showed a total sales of $8.9 billion in 2001, of which Unilever, P&G, and Colgate-Palmolive had a market share of 33, 11, and 10%, respectively, while the key leading global brands were Lux (10%), Dove (9%), and Palmolive (4%). A slightly different estimate of the worldwide toilet-soap-bar market values the global retail value as U.S. $9.6 billion, and the estimate is that about $1.4 billion is claimed by syndet and combo bars (Hendrickx, 2002).

The 2007 figures follow the same trend globally, but differences are found by geographical areas. As many other things, the soap business is also a matter of geography. According to the *Euromonitor* statistics, the total retail-sales value of the global soap market summed up in 2007 to U.S. $10 billion. The key leading brands were, as in 2001, Lux (12%), Dove (11%), and Palmolive (4%). To this list, worthy of mention is Zest, the combo of our interest, with a global share of 2% (IFF, 2008a). The increase of the total global-soap-market sales, by 11.1% from U.S. $8.9 billion in 2001 to $10 billion in 2007, seems surprising for a shrinking soap-bar market.

However, if we consider the influence of the other geographical areas, the reason seems obvious. The Asia–Pacific area, that had in 2007 a retail sales value of U.S. $3.4 billion, is characterized by a much higher consumption of bar soaps. For instance, the Indian bar soaps account for about 80% of the total body-wash sales, amounting to U.S. $1.3 billion. The same figures of higher bar-soap consumption compared to total liquids and gels characterize, as well, the Eastern European, as compared to the Western European market. Updated available figures of solid and liquid soap consumption in Europe are presented in Table 4.13. All data compared *Euromonitor* figures between 2001 and 2007 (IFF, 2008a, 2008b, 2008c), except for Russia, where 2005 figures were available (Symrise, 2005).

The 2007 bar-soap consumption in Western Europe, compared to 2001, decreased 18% in France, 20% in Germany, 25% in Italy, and 38% in the United Kingdom against the use of liquid soaps and shower gels. In Russia and Turkey, bar-soap consumption has been steady for the time being. However, not like the classical bar-soap situation, the syndet/combo bar market in Western Europe reveals a more positive situation. This is due mainly to Dove's impressive market penetration and the use of specially formulated medicated-type syndet and combo bars.

According to *Datamonitor* data, during 2000–2001, Dove became the leader in France, Italy, and the United Kingdom with market shares of 16.7%, 13.6%, and 21.5%, respectively (Symrise, 2003). However, except for Sebamed, with a market share of 4.3% in Germany, no other syndet/combar was a leading brand (Symrise, 2003).

Table 4.13 Solid and Liquid Soap Markets in Europe (2001–2007)

	Bar Soaps		Liquid Soaps		Shower Gels	
	2001	**2007**	**2001**	**2007**	**2001**	**2007**
France	132	108	65	90	385	440
Germany	100	80	95	95	470	450
Italy	160	120	130	140	160	180
Spain	31	30	13	14	230	340
United Kingdom	210	130	95	145	330	450
Turkey	55	78	—	—	—	—
Poland	61	59	—	—	—	—
Russia	347	434	—	—	—	—

Note: Sales revenue in million Euro.

Sources: IFF, 2008a, 2008b; Post et al., 1997.

Table 4.14 Market Shares (%) of European Bar Soaps (2006)

	France	Germany	Italy	Spain	United Kingdom
Dove (Unilever)	16.4	11.8	23.0	16.6	27.6
Le Petit Marseillais (Lab Vendome)	11.7	—	—	—	—
Monsavon (Sara Lee)	7.1	—	—	—	—
Palmolive (Colgate)	5.1	5.6	12.7	7.4	4.1
Nivea (Beiersdorf)	4.0	10.5	—	—	—
CD (Lornamead)	—	9.7	—	—	—
Lux (Unilever)	—	7.9	—	—	—
Sebamed (Sebapharma)	—	4.3	—	—	—
FA (Henkel)	—	7.6	—	—	—
Atkinson (P&G)	—	—	10.5	—	—
Neutro Roberts (Manetti & Roberts)	—	—	8.8	—	—
Fiori Roberts (Manetti & Roberts)	—	—	2.9	—	—
Heno de Pravia (Perfumeria Gal)	—	—	2.4	21.7	—
La Toja (Henkel)	—	—	—	10.5	—
A-Derma (Pierre Fabre)	4.9	—	—	1.2	—
Spuma di Sciampagna (Italsilva)	—	—	—	5.6	—
Magno (Henkel)	—	—	—	2.7	—
Imperial Leather (Cussons)	—	—	—	—	17.6
Simple (Accantia)	—	—	—	—	4.5
Pearl (Cussons)	—	—	—	—	3.5
Tesco (Tesco)	—	—	—	—	3.9
Neutromed (Henkel)	—	—	—	—	2.2
Johnson & Johnson pH 5.5 (J&J)	—	—	—	—	1.9

The 2006 market shares of the leading European bar soaps are presented in Table 4.14 (IFF, 2008a). Dove dominates in all the five listed countries. The French syndet-bar market is active, offering various formulations and functional variants; among them are: A-Derma (Laboratories Ducray), Klorane–Dermo (Laboratories Klorane), Avene (Laboratories Ducray), and Vendome (Laboratories Vendome).

Future Trends

Milder formulations with enhanced skin-care properties targeted to offer an aesthetic, consumer-appealing appearance seem to be a major trend in the future. The emphasis on environmental care and the use of natural renewable raw materials, made exclusively from vegetable-based fatty materials, will continue to drive development.

A transparent neutral syndet—perceived by customers as a pure product, free of any harmful ingredients—will also be targeted as a specialty bar. A transparent, extrudable neutral syndet, of reasonable cost and performance, should be a supreme challenging target.

During the last few years, bar soaps evolved into more complex products that must satisfy multiple functional needs (hygiene, antibacterial protection, skin care, mildness, and crossover) and emotional pleasures (well-being, attractive shapes, decorative look, and packaging) (Branna, 2001; Emsley, 2002; Marchie, 2001). The realization of these challenging targets, creating "new sensations in soap" and "wow" products, will drive new marketing strategies and continuous innovation, which nowadays are more important than ever for the future market of bar soaps.

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5

Transparent and Translucent Soaps

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Introduction

Transparent and translucent soaps have a surprisingly long history. It was discovered at least as far back as 1789 that a transparent soap bar could be made by dissolving soap in hot ethyl alcohol, pouring the mixture into open molds to solidify, and then allowing the soap to age (Cristiani, 1881). Well over two centuries later, transparent and translucent soaps make up a good proportion of soap bars sold in the marketplace. They are sold in a variety of shapes and degrees of optical clarity, and some are hand-crafted by artisans, whereas others are mass-produced by the large soap manufacturers. However they are made, these soap bars have much consumer appeal, as clarity in a soap bar connotes health, purity, mildness, and freshness.

Although transparent soaps have far greater optical clarity than translucent soaps, they do share some commonalities. All compositions contain mostly tallow and coconut soap, and they can also include varying levels of soaps made from castor oil, safflower oil, or synthetic detergents. In addition, unlike ordinary soap bars, which are generally exclusively sodium soap, transparent and translucent soap bars both typically contain mixtures of sodium, potassium, and/or triethanolamine soaps. Finally, both transparent and translucent soap bars generally contain polyols, such as glycerine, propylene glycol, sorbitol, or sucrose.

The manufacturing process for transparent soaps differs from that for translucent soaps. Translucent soaps are manufactured by energetic working, which easily lends itself to mass production on a standard soap manufacturing line that has been modified to allow for this. In contrast, transparent soaps are manufactured by preparing and casting a melt, followed by cooling and solidification and sometimes by additional aging, a process that cannot be used in a standard soap finishing line.

In this chapter, we provide a coherent understanding of the relationships and interdependencies between optical clarity, bar composition, processing route, and processing parameters. First we build on basic concepts of soap phases and structure to identify sources of light scattering, and we show how molecular interactions amongst the components of a soap bar are critical to the development of optical clarity. Then we discuss the importance of the process path and how it affects the efficiency of molecular interactions.

Soap Structure and Transparency Development

To understand why soap bars may be more or less transparent, we need to consider how the various features of a soap bar can impact the transmission of light. For example, surface

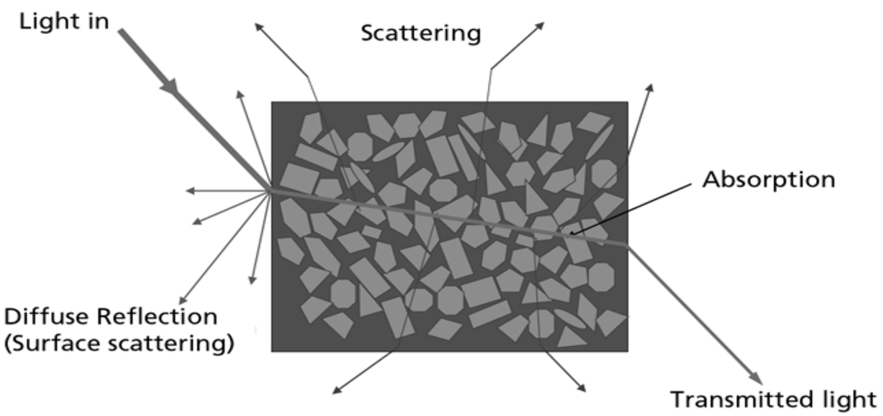

Figure 5.1 Possible sources of interaction of a soap bar with light.

imperfections will cause surface light scattering, decreasing the intensity of transmitted light. Internal objects that are larger than 200 nm will also scatter light and thereby reduce the transmitted light intensity. In addition, the presence of any objects that can absorb the incident light beam will also reduce the transmitted light intensity. These possible sources of interaction of soap with light are depicted in Figure 5.1.

Applying these general principles of light transmission through soap requires an understanding of the various phases present in a soap bar. As indicated in Chapter 2 of this book by Hill and Moaddel (2004), commercial soap bars generally contain multiple components divided among multiple phases, and the particulars of the distribution of components across the phases depends on the oil blend and the process route that are used to get to the final structure. In conventional extruded toilet soap, a mixture of two separate crystal types forms at thermodynamic equilibrium. One crystal type, referred to as *delta phase*, is composed of the less soluble saturated long-chain soaps (e.g., C16 and C18 soaps) and is dispersed in a continuum of another crystal type composed of the more soluble saturated short-chain soaps and unsaturated soaps (e.g., C12 and C18:1 soaps), referred to as *eta phase*. The configuration of less soluble soaps dispersed in a continuum of more soluble soaps can be compared to bricks and mortar, as depicted in Figure 5.2.

The continuous phase (the mortar), which is composed of the more soluble soaps, will also contain more water than the dispersed phase (the bricks), which is composed of the less soluble soaps. Further, because solid soap and water have different refractive indices ($n \approx 1.5$ for solid soap, $n = 1.0$ for water), these two phases will have different refractive

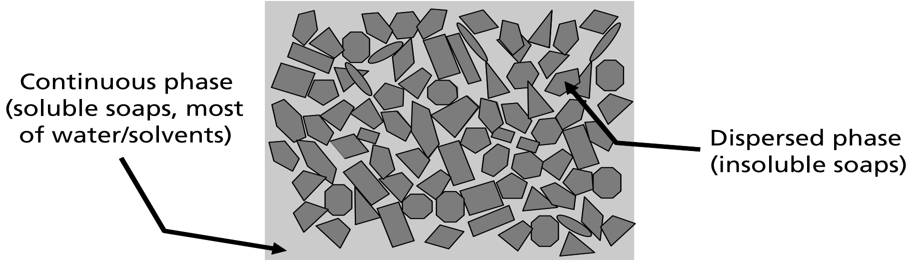

Figure 5.2 Brick and mortar structure of a soap bar.

indices. Thus, incident light can be scattered as it passes through the different phases in the soap bar. Large dispersed soap crystals, entrapped air, and surface roughness will also scatter light, and dark objects present in the soap bar will absorb light.

This suggests that to maximize light transmission, the soap formulator should endeavor to raise the refractive index of the continuous phase, reduce the size of solid soap crystals, minimize entrapped air, reduce surface roughness, and keep the color light. The latter three can be regarded as trivial, and we will not focus on them here. The former two, however, relate to soap solubilization and soap crystal size. Since a soap bar can consist of multiple components distributed amongst multiple phases, controlling these two parameters is nontrivial.

Typical Soap Phases, Their Properties, and Methods for Characterization

The more commonly encountered soap phase structures in a commercial soap bars can be illustrated in the generic binary phase diagram of soap and water, depicted in Figure 5.3. The various concentrated soap phases can be classified into two main groups: solid crystals and liquid crystals.

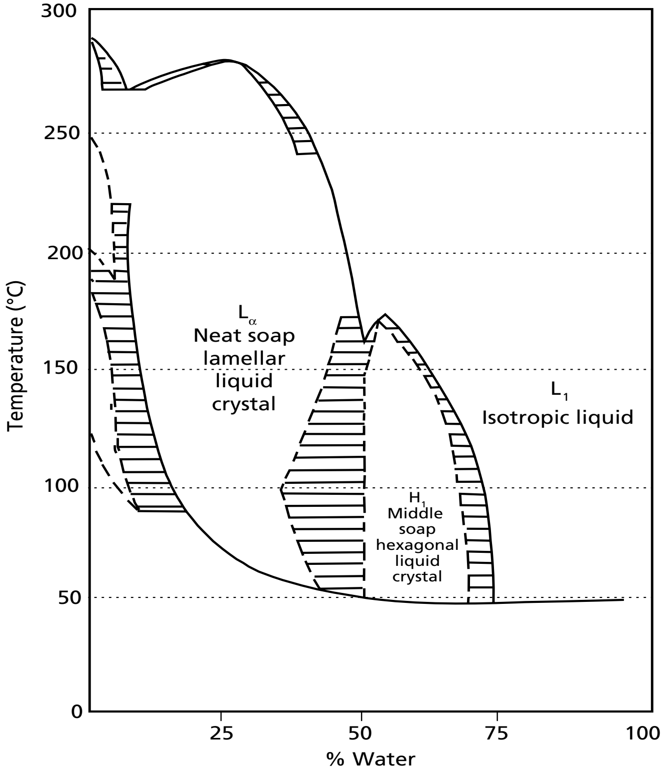

Figure 5.3 Generic binary phase diagram of soap and water. Reprinted from Hill and Moaddel, 2004.

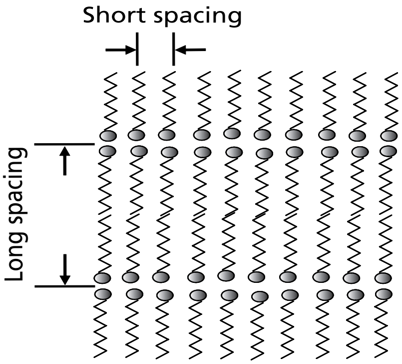

Figure 5.4 Structure of solid soap crystals.

The structure of solid soap crystals is depicted in Figure 5.4., and it corresponds to packed bilayers of soap molecules. As Chapter 2 describes in greater detail, the more common soap phases have been described using two sets of nomenclature; see Table 5.1. Typical liquid crystal phases encountered in commercial soaps include the lamellar liquid crystal phase and the hexagonal liquid crystal phase, depicted in Figure 5.5.

The lamellar liquid crystal phase, L_α, is similar to that of solid soap crystal, as both have soap molecules arranged in planar sheets. However, the hydrocarbon tails in the liquid crystal are in a "fluid" state, whereas the hydrocarbon tails in the solid crystal are in a "rigid" state. On the other hand, the more viscous hexagonal liquid crystal phase, H_1, consists of close-packed long cylindrical micelles with the soap molecules aligned so that the hydrophilic heads are on the cylinder surface and the hydrophobic tails point toward

Table 5.1 Common Soap Phases

Ferguson	Buerger	Phase
Omega	Kappa	Disordered mixed crystal with all chain lengths, saturated
Omega	Eta	Mixed crystal rich in unsaturated and short chain saturated soap
Beta	Zeta	Small mixed crystals rich in long chain saturated soap
Delta	Delta	Large mixed crystals rich in long chain saturated soap

Sources: Buerger et al., 1945; Ferguson et al., 1942; Ferguson, 1944.

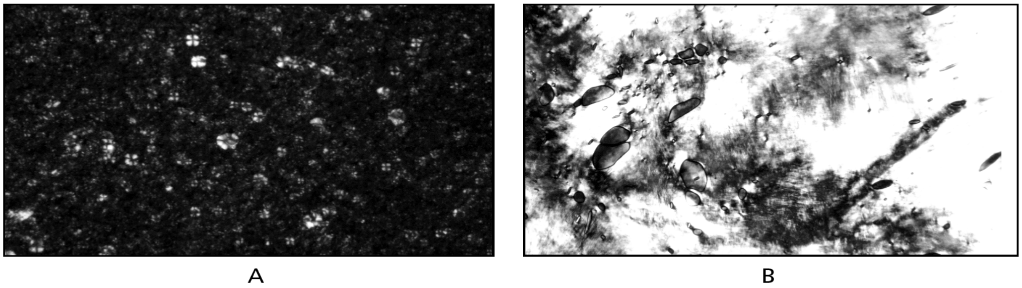

Figure 5.5 Photomicrograph of lamellar liquid crystal (A) and hexagonal liquid crystal (B).

the center. We refer the reader to Chapter 2 for more details. Optical microscopy with cross-polarizers, differential scanning calorimetry, small angle X-ray diffraction, and rheology are typical characterization tools used to investigate the structural nature and flow behavior of these different phases (Nemeth et al., 1998; Funari et al., 1992; Ahir et al., 2002; Rosevear, 1968; Borne et al., 2000; Laughlin et al., 1994).

Translucency Development during Neat Soap Drying and Finishing

Vacuum Spray Drying

Vacuum spray drying of neat soap rapidly converts the lamellar liquid crystalline phase to solid soap crystals. The thermodynamically preferred distribution of the various soaps has all the insoluble (long-chain saturated) soap in the bricks and all the soluble (short-chain and long-chain unsaturated) soap in the mortar at equilibrium. However, the viscosity of the neat soap imposes a mass transfer limitation onto the individual soap molecules during the drying process, preventing their migration to their preferred equilibrium phases. Thus, soluble and insoluble soaps are often trapped together as one solid soap crystal, a metastable situation. This is depicted in Figure 5.6. The extent of this entrapment depends critically on the final water level of the spray-dried pellet, and for optimum translucency development using the minimal amount of energetic working, the final moisture in the soap noodles should typically be no less than 16%. Above 16% moisture a phase transformation takes place that renders a microstructure more amenable to translucency development.

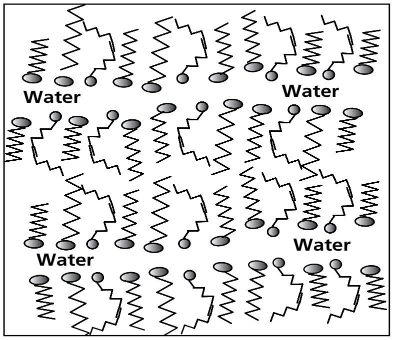

Figure 5.6 Metastable solid soap crystals.

Intensive mechanical mixing of the spray-dried soap pellets can create sufficient surface renewal to overcome the mass transfer limitation, allowing the soluble soaps to redissolve or melt while leaving behind the insoluble soaps to recrystallize as zeta (beta) phase soap crystals. This is desirable in the manufacture of translucent soaps for two reasons. First, increased levels of soap dissolved in the continuous phase will raise its refractive index to more closely match that of the dispersed phase, and second, zeta (beta) crystals are smaller than other solid soap crystal forms. Both effects increase the transmission of light through the bar.

However, this recrystallization will occur only if the zeta (beta) phase is favored at the temperature and water levels experienced during mixing. For example, under conditions of low moisture and temperature (below 13% and below 40 °C), short-chain and unsaturated-chain soaps will not redissolve, and this recrystallization will not occur. At the other extreme, if the moisture and temperature are too high (above 18% and 50 °C, respectively), as can be encountered during downstream soap-making operations (i.e., roll mills and plodders), the short-chain and unsaturated-chain soaps will not crystallize until the system cools sufficiently, and the long-chain soaps will crystallize as either kappa (omega) or delta phase soap rather than zeta (beta) phase. Thus, the *operating window* for translucency development spans conditions that are hot and wet enough for the unsaturated and short-chain saturated soaps to melt or dissolve into the liquid crystal, but cool and dry enough for the long-chain saturated soaps to remain insoluble. This is depicted in Figure 5.7.

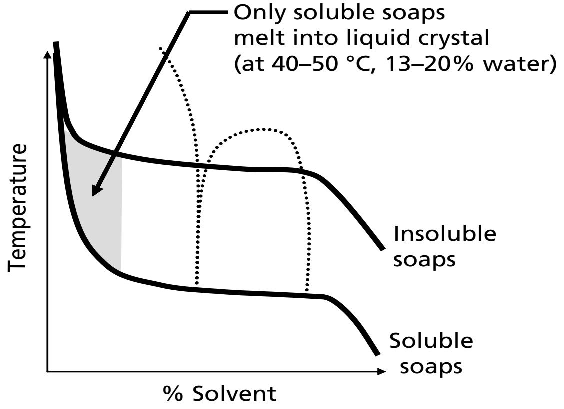

Figure 5.7 Operating window for translucency development.

The development of translucency largely depends on how well formulation ingredients and processing equipment facilitate the recrystallization of the kappa (omega) phase into the zeta (beta) phase. One approach to achieving this recrystallization involves adding solubilizers. Solubilizers raise the solubility of the short-chain and unsaturated-chain soaps, thereby facilitating recrystallization into zeta (beta) phase soap. Since solubilizers also have a high refractive index, their presence raises the refractive index of the continuous phase, which is desirable for translucency. Effective solubilizers include glycerine, propylene glycol, sucrose, sorbitol, and triethanolamine.

The choice of soap counter-ion and tail group can also affect the development of translucency by promoting disruption of crystal packing, leading to smaller and fewer solid crystals. For example, going from sodium to potassium to triethanolamine, the counter-ion becomes larger and crystal packing is more easily disruptable, due to the increasing area occupied by the hydrophilic head group, as shown in Figure 5.8. Similarly, if the fatty tails of the soap molecules are unsaturated or branched, this also disrupts crystal packing by increasing the volume of the hydrophobic portion, as shown in Figure 5.9.

One final and sometimes overlooked factor necessary for translucency development is a proper ratio of short-chain to unsaturated-chain soaps. The solubility of short-chain and unsaturated soaps depends greatly on this ratio. Figure 5.10 depicts the phase behavior of a mixture of sodium laurate and sodium oleate as a function of the ratio of oleate to laurate. The water solubility of the mixture is greatest at a molar ratio of 1:1. Since translucency

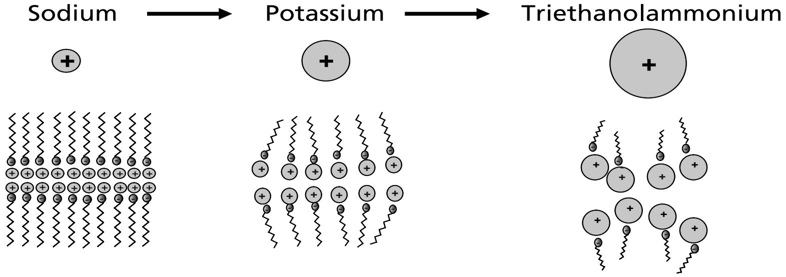

Figure 5.8 Effect of soap counter-ion on crystal packing.

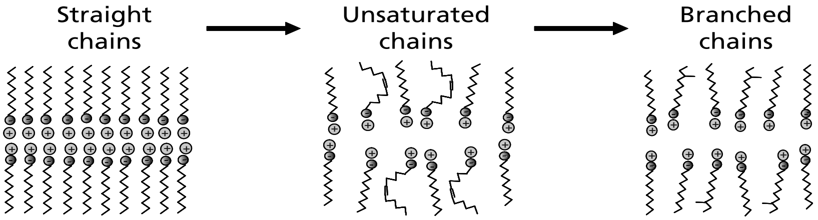

Figure 5.9 Effect of soap hydrophobic tail group on crystal packing.

requires recrystallization into zeta (beta) phase, and this is facilitated by increasing the solubility of the continuous phase, translucency should be best at an oleate:laurate molar ratio of 1:1. This corresponds to a tallow:coconut ratio of between 90–10 and 65–35, respectively, or an IV of between 30 and 50.

Thus, production of translucent soap with excellent optical clarity requires 70–80% soap with an IV between 30 and 50; 5–12% of a combination of polyols, which can include select mixtures of glycerine, propylene glycol, and sugars; and 13–20% water, combined with sufficient intensive mixing within the right window of temperature and water levels (typically 40–50 °C and 13–20% water).

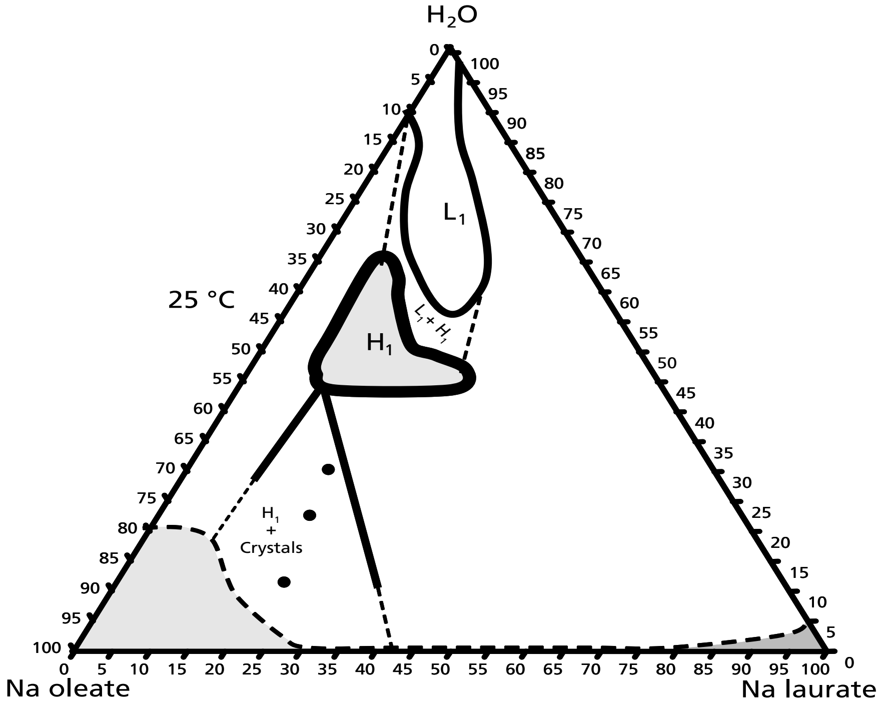

Figure 5.10 Phase diagram of sodium oleate, sodium laurate, and water.

L1—Isotropic micellar phase; H1—Hexagonal liquid crystalline phase. Reprinted from Mongondry et al. (2006).

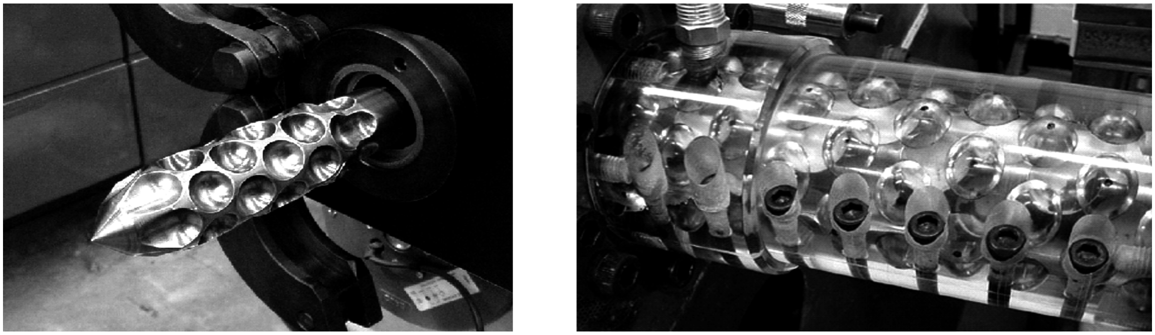

Figure 5.11 Cavity transfer mixer.

Intensive Mixing and Refining

The choice of intensive mixing equipment is also critical for achieving translucency. Double-arm mixers are the most widely used intensive mixing equipment. A very interesting unit that was used in the past, but has not gained wide acceptance, is the cavity transfer mixer (Figure 5.11).[1] Each has its advantages and disadvantages.

In all cases, all nonsoap ingredients can be added to standard opaque soap pellets, provided adequate distributive and intensive mixing are achieved. The double-arm mixers and special plodders (see Chapter 8) can meet both these needs, and using them is logistically the simplest approach. Adding the specific polyol blend to the neat soap prior to spray-drying is a more efficient means to incorporate polyols into soap. By this route translucency development is greatly enhanced as a result of better molecular solubilization of polyols and soap. The degree of translucency of the spray-dried pellets (noodles) produced depends on the number of plodders of the vacuum spray-drying system.

The combination of added polyols and the mechanical work imposed on the system generates the right phase sequence and colloidal structure for effective translucency development for extruded bars. By this route, no further intensive mixing or work is required for translucency development as spray-dried pellets are already translucent. This route, although providing better translucency development, is logistically more complex. It is the combination of added polyols with intensive mixing that dissolves the soluble soap fraction of the metastable solid soap crystal that is generated at the spray-drying stage, leaving the insoluble soaps to recrystallize as zeta (beta) phase soap and resulting in a colloidal structure amenable to translucency development. The more efficiently this separation is accomplished, the better the translucency development. These results reflect the strong interplay between the various polyols and the soap that drives the development of translucency (Wang et al., 2004). Figure 5.12 is a phase diagram of the soluble soap fraction of a typical soap bar with water and glycerine at 45° C,[2] and this illustrates this association between soap and polyol.

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[1] In the Cavity Transfer Mixer the intensive work occurs between rotor and stator, which provides for a continuous operation, and it is enclosed and jacketed, which provides good temperature and moisture control.

[2] The L_1 phase has been determined to be within 5%. The exact phase boundaries were not accurately determined for the more viscous phases and are only estimates.

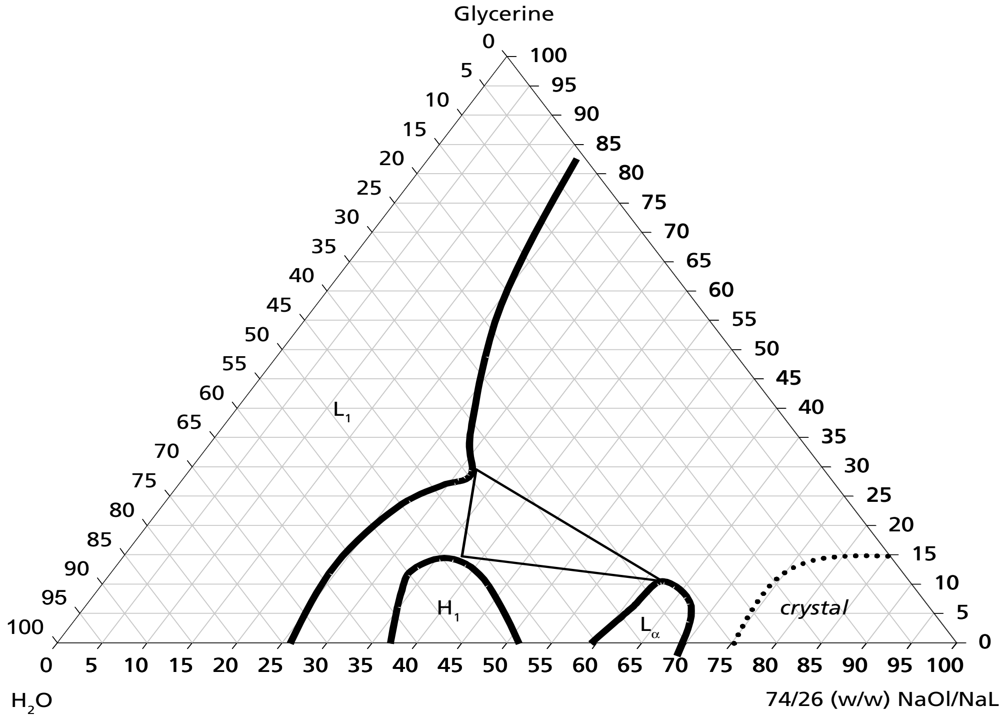

Figure 5.12 Phase diagram of glycerine, water, soluble soap fraction of soap.
L_1—Isotropic micellar phase; H_1—Hexagonal liquid crystalline phase; L_α—Lamellar liquid crystalline phase; NaOl—Sodium oleate; NaL—Sodium laurate.

Clearly evident is the formation of association structures between glycerine, water, and soap and the extension of the isotropic micellar phase, L_1, from the water corner of the phase diagram to the glycerine corner of the phase diagram. This specific interaction of glycerine with soap is fundamental to understanding why and how soaps can be made translucent or transparent.

It follows from the previous discussion that the fat source directly affects translucency development. In particular, changing the fat source from animal fat to vegetable fat changes the inherent fat composition. This incurs the following major changes:

- A decrease in the level of C18 saturated soap at the expense of increasing C16 saturated soap
- Increased levels of C18:2 (linoleic acid)

Cast-Melt Process and Transparency Development

Pears, the World's First Transparent Soap, was introduced in 1789. It contained glycerine, natural oils, rosemary, cedar, and thyme. The process by which these bars were made involved pouring saponified oils and additives into molds. These were then cut and allowed to mature for a period during which the alcohol evaporated and was recovered for reuse.

The final bars were then stamped. The key ingredient helping to render these bars transparent was ethanol, which acts as a hydrotrope. That is, the addition of ethanol increases the solubility of the soap and prevents the liquid crystal phase from forming when the soap solution is cooled. In this case, when the soap solution cools, it forms a gel structure rather than the usual bricks-and-mortar structure. It is still debated whether the structure of these bars is a gel consisting of a rigid network of small solid crystals with isotropic solution in the interstices, or instead consists of a supercooled solid (a "glassy state") with dispersed solid crystals (Wang et al., 2004). Other approaches to making transparent melt-cast soap bars involve the use of high levels of polyols, such as glycerine, propylene glycol, various sugars, and triethanolamine, to increase soap solubility and prevent liquid crystal formation on cooling. In contrast to the methods in which ethanol is used, there is no need for maturation. The patent literature also shows that highly soluble syndets, such as sodium lauryl ether sulfate, sorbitan oleate, nonyl phenol ethoxylates, and sodium cocoyl isethionate, are often used to make transparent soaps. In these cases, however, soap remains the primary structurant. Transparent soap bars of excellent optical clarity can be made by combining 35–50% soap (with minimal unsaturation), 30–40% specific blends of polyols, and 15–25% water. The soap used in these compositions must have a minimum level of unsaturation so as not to promote formation of the liquid crystalline phase on cooling.

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6

Semi-Boiled and Integrated Saponification and Drying Systems

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Introduction

There are two major soap processing systems based on not-extracted and extracted glycerine:

- Not-extracted glycerine processes: Soap With Included Glycerine (SWING)
  - Integrated saponification and drying
  - Semi-boiled
- Extracted glycerine processes: Soap After Glycerine Extraction (SAGE)
  - Continuous saponification
  - Full boiled

Semi-boiled saponification is the oldest SWING type process, and it is still widely used for laundry soap and economy-grade multipurpose soaps. In this process, the glycerine contained in the fats and oils produced by the saponification reaction remains in the base soap (Figure 6.1).

As glycerine prices dropped over the last decade, it became unprofitable for soap producers to recover glycerine. As a result, the soap industry has been adopting the SWING technology for toilet and laundry soap production worldwide.

This chapter will cover the not-extracted glycerine SWING processes.

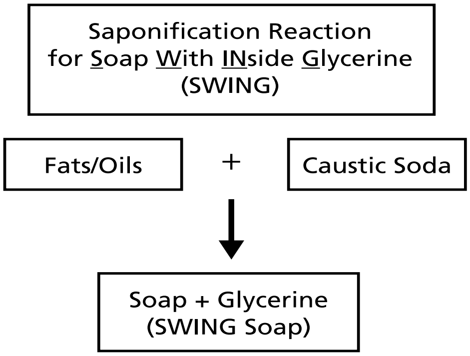

Figure 6.1 Saponification reaction.

Traditional and Current Technology

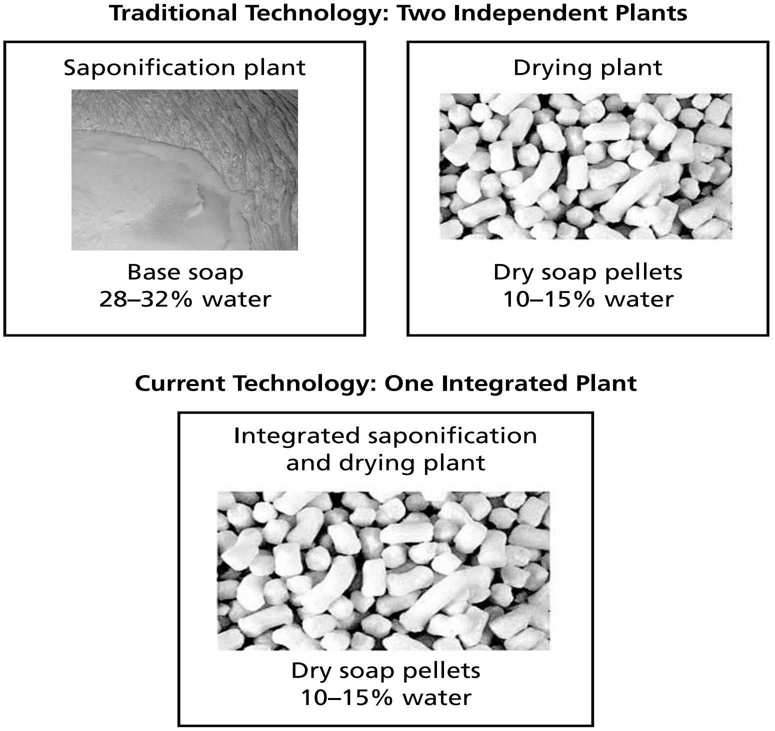

Figure 6.2 Traditional and integrated soap processing systems.

Traditional and Current Technology Yield Comparison	
1000 Kg of Fats and Oils	
Traditional process	**Semi-boiled process**
Yield: 1,200 Kg dry soap pellets	Yield: 1,350 Kg dry soap pellets
Composition	
70–72% TFM 13–15% Water 0.5–0% Glycerine 0.04–0.06% NaOH 0.6–0.6% NaCl	78–80% TFM 13–15% Water 7–8% Glycerine 0.04–0.06 % NaOH 0.6–0.6% NaCl

Figure 6.3 Traditional and current process yield comparison.

Total Fatty Matter (TFM) and Water Content

Total fatty matter (TFM) and water content analysis are very important for quality control purposes. TFM analysis requires laboratory equipment and skill. Water content (moisture) is determined with a simple moisture analyzer used in the laboratory and alternately can be easily used on the manufacturing floor by an operator. Water content determination is the preferred method used by most producers.

Table 6.1 summarizes the data for base soap (neat soap) and dry toilet soap pellets with glycerine and without glycerine. (For more information on TFM, refer to Chapters 7 and 12.)

Saponification plants produce 28–32% water content liquid base soap (also called neat soap). Vacuum spray drying plants convert the liquid-base soap into dry soap pellets containing 10–15% water. These two plants can operate separately from each other or combine into a single integrated system for the production of SWING soap.

Table 6.1 TFM and Water Content

	Base Soap			**Dry Soap Pellets**		
	% Water	**% TFM (SWING)**	**% TFM (DFA)**	**% Water**	**% TFM (SWING)**	**% TFM (DFA)**
Standard	28–32	58–54	66–62	19–23	66–63	74–71
Semi-concentrated	22–28	64–58	72–66	13–19	72–66	80–74
Concentrated	18–22	67–64	75–72	9–13	75–72	83–80

Notes:

TFM (SWING): Value obtained by saponifying fats and oils, generating 8% glycerine.

TFM (DFA): Value based on neutralization of distilled fatty acid mixtures without generating glycerine.

The data assumes that the dry toilet soap pellets contain: 8% glycerine, 0.04% NaOH and 0.4% NaCl.

Integrated Saponification and Drying Processing Plants for SWING Soap Production

Binacchi & Co., Mazzoni LB, SpA, SAS, and Soaptec Srl are the most widely used SWING soap processing plants. The different reactor designs by each manufacturer and the detailed processes will be described.

There are many advantages in installing and operating integrated plants:

- Low capital cost compared to other systems
- Reduced manufacturing cost
- 7–8% of glycerine remains in the neat soap
- No washing, no neat soap and spent lye separation
- No glycerine treatment, evaporation, and refining plants
- No need for neat soap holding tanks
- Wide range of raw materials usage

- No final alkalinity adjustment
- Zero steam consumption
- Savings in electric energy and cooling water
- Compact layout
- Simple and flexible operation
- Fast and easy formula changeover
- Lower operator skill level requirements
- Simple quality control requirements
- No byproducts, resulting in lower environmental impact
- Reduced soap fines formation and cooling water entrainment

Binacchi MPSD Integrated Saponification and Drying Plant

The Binacchi MPSD integrated plant consists of two plants integrated into a single combine (Figure 6.4). The saponification section is designed for the continuous saponification and neutralization of fats and oils and fatty acids, or admixtures of both.

The plant is designed to saponify neutral fats-oils (tallow, palm oil, coconut oil, palm kernel oil, palm stearin, etc.), and neutralize fatty acids alone or any fats and oils and fatty acid mixture. The semi-concentrated soap base (neat soap) is dried into soap pellets in the vacuum spray dryer.

Saponification Section

- Filtered water, caustic soda, fats and oils, and fatty acids are fed from storage tank dosing pumps.
- Two different dosing lines of fats and oils and fatty acids allow for easy changes to the soap composition.
- Multihead additive pump doses brine, chelants, and other minor additives.
- A water addition system is included to allow for the use of commercial 50% caustic soda solution.

The dosing pumps are controlled by frequency inverters that receive signals from flow meters, ensuring a very precise amount of dosed raw materials.

Before the reaction, the raw materials are mixed with static mixers, heated in preheaters and emulsified in the first turbo mixer. The reaction takes place inside a rotating multiblade reactor with internal agitator (Figure 6.5, p. 122).

Continuous soap recirculation ensures a very effective catalyst and intensive mixing in the reactor, and soap recirculation guarantees complete saponification.

Drying Plant

Liquid neat soap is sent directly to the drying section to produce dry soap pellets. The neat soap storage tank, feed tank, vapor separator, and heat exchanger are no longer required because the liquid soap is fed at low moisture (semi-concentrated liquid neat soap); thus, the evaporation under vacuum can reach any required final soap pellet moisture. For details on drying, see Chapter 7.

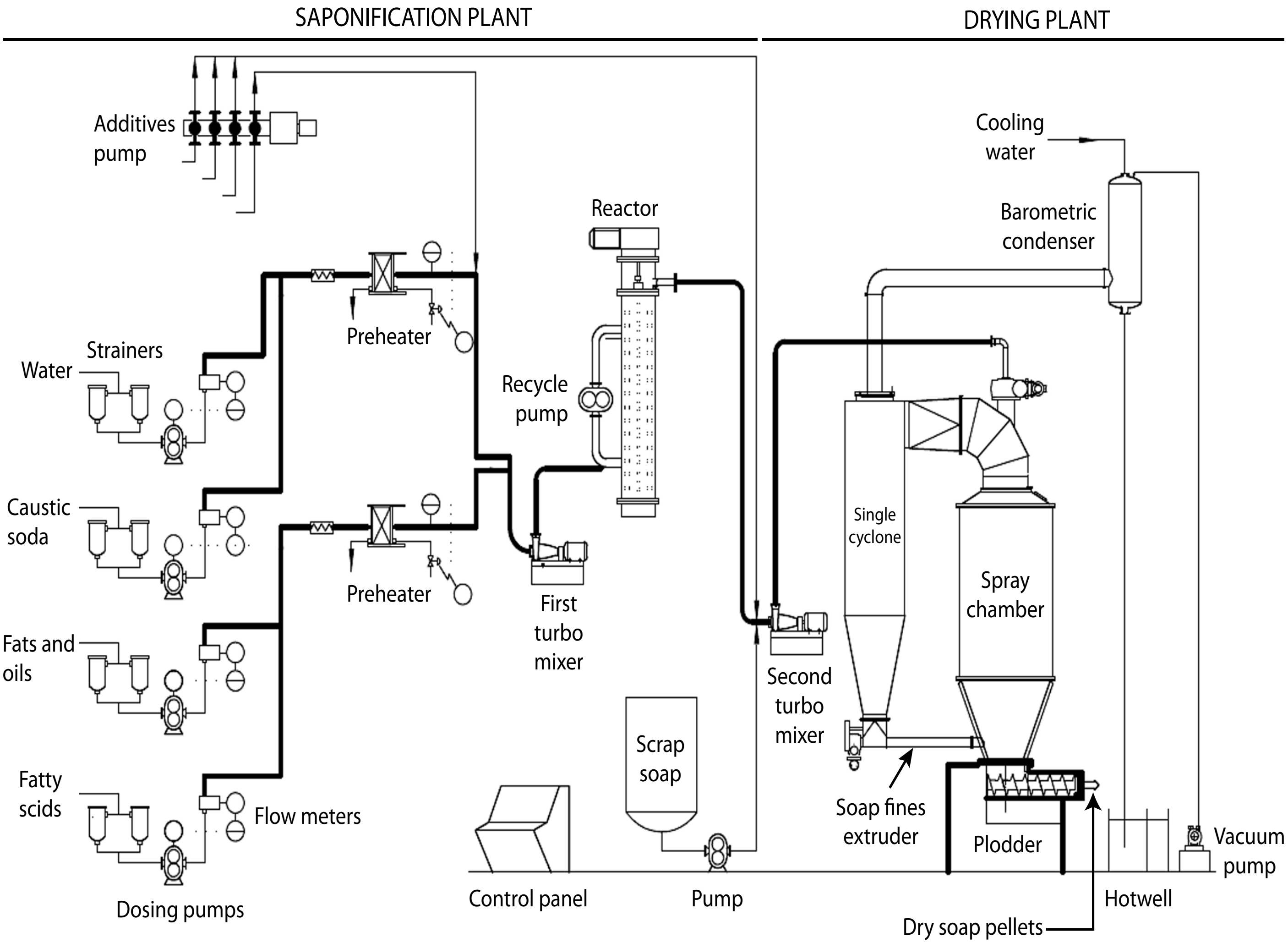

Figure 6.4 Binacchi MPSD integrated plant.

Source: Binacchi & Co.

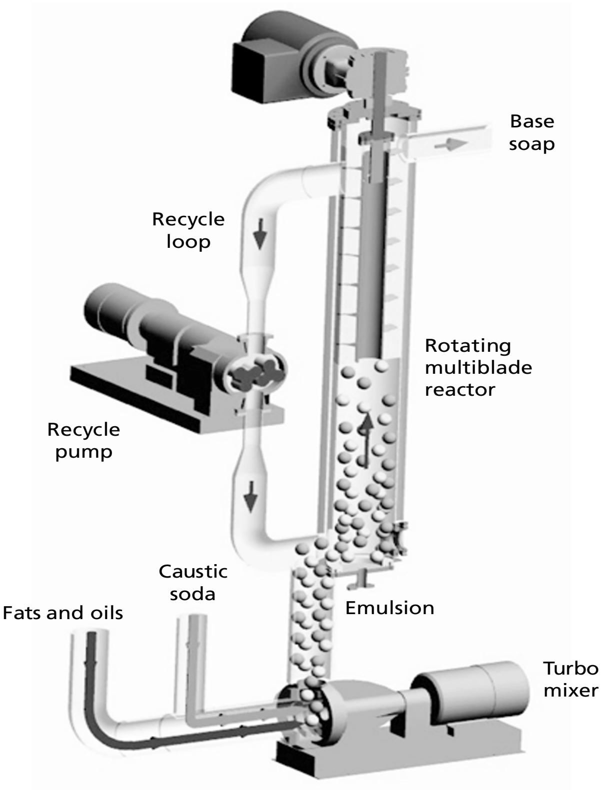

Figure 6.5 Binacchi multiblade reactor.
Source: Binacchi & Co.

Binacchi Multiblade Reactor

The vertical jacketed reactor with a rotating multiblade agitator is fed with the emulsion formed in the turbomixer. The intensive mixing by the multiblade combined with a high volume recycle of the soap, guarantees complete saponification of all types of raw materials. Fully saponified wet base soap is discharged from the top of the reactor.

Mazzoni LB Integrated Toilet Soap Pellets Production Plant

An integrated plant for the production of 10–15% water content dry toilet soap pellets is illustrated in Figure 6.6. The plant consists of: raw materials feed groups, saponification loop, vacuum spray drying plant, and optional additive group. Fats and oils are preheated in a plate heat exchanger with low pressure steam. Caustic soda diluted with process water in an in-line static mixer is also preheated. Brine and chelant solution are dosed by piston dosing pumps at room temperature. All the materials are fed into the turbodispenser and the reactor of the saponification loop. A recycle pump completes the loop. The base soap from the reactor is sent directly to the “no spray” vacuum chamber. The flow sheet shows that this plant can be used for the neutralization of fatty acids. Refer to Chapter 7 for details.

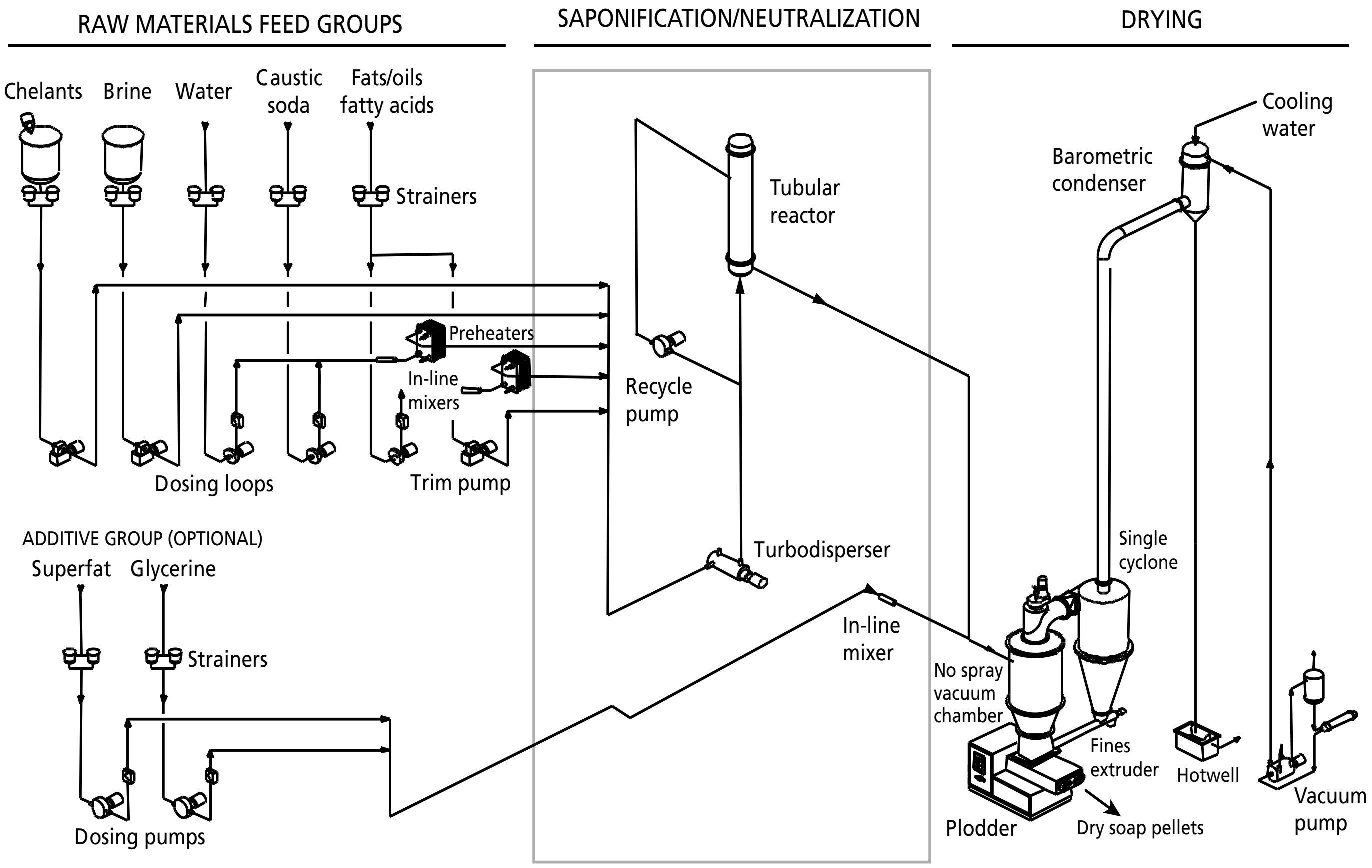

Figure 6.6 Mazzoni integrated plant for toilet soaps.

Source: Mazzoni LB SpA.

Mazzoni LB Tubular Reactor and Saponification Loops

Tubular Reactor

The tubular reactor (Figure 6.7) is a static jacketed reactor without any moving parts. The operating conditions in the reactor are: 2–3 barg pressure and 115–120 °C temperature. Depending on the raw materials, the residence time varies from 10 to 20 minutes.

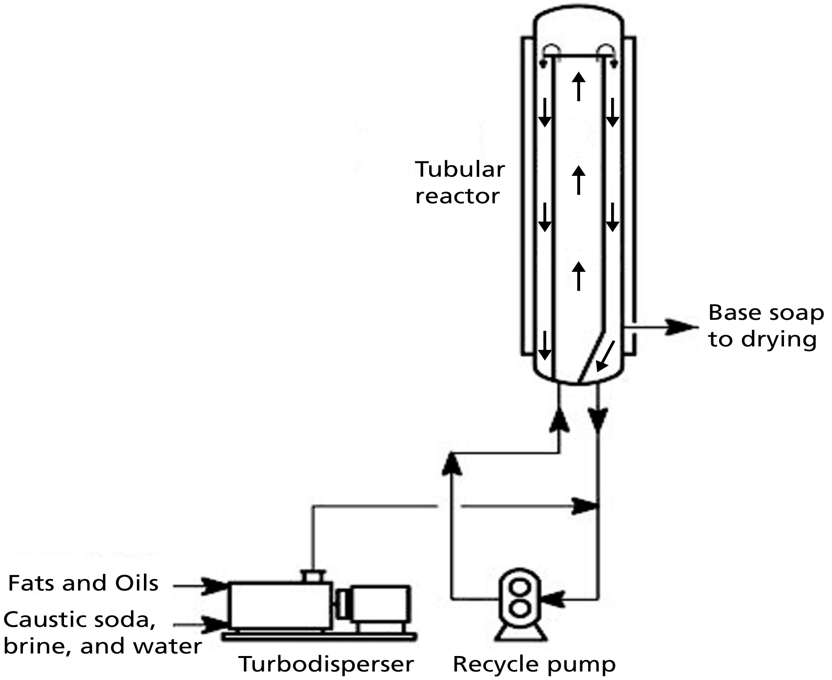

Figure 6.7 Mazzoni LB tubular reactor.
Source: Mazzoni LB SpA.

Saponification Loops

The reactor uses two saponification loop configurations according to base soap water content requirement for toilet and laundry soaps (Figure 6.8).

Saponification Loop for 20–24% Water Content Base Soap

The saponification loop consists of a positive displacement (PD) type recycle pump with a recycle loop, a high shear turbodispenser, and a tubular reactor. Soap from the reactor is sent directly to the vacuum chamber for all type of soaps. This loop is used for laundry soap production.

Saponification Loop for 28–32% Water Content Base Soap

This saponification loop consists of an open-impeller centrifugal type recycle pump, a tubular reactor, and a recycle loop. Base soap from the reactor is fed directly to the vacuum chamber for toilet soap production.

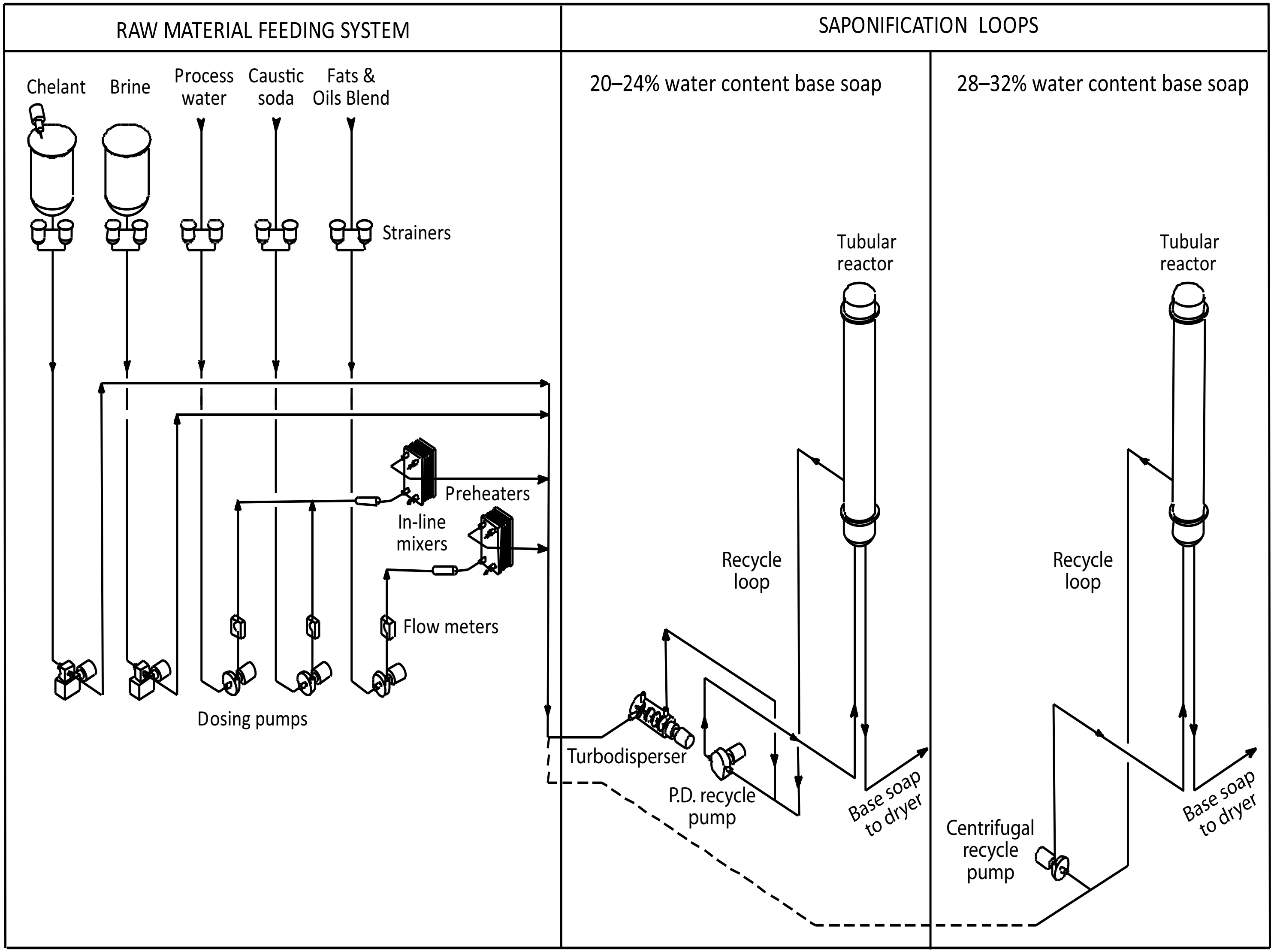

Figure 6.8 Mazzoni LB Tubular Reactor Applications.

Source: Mazzoni LB, SpA.

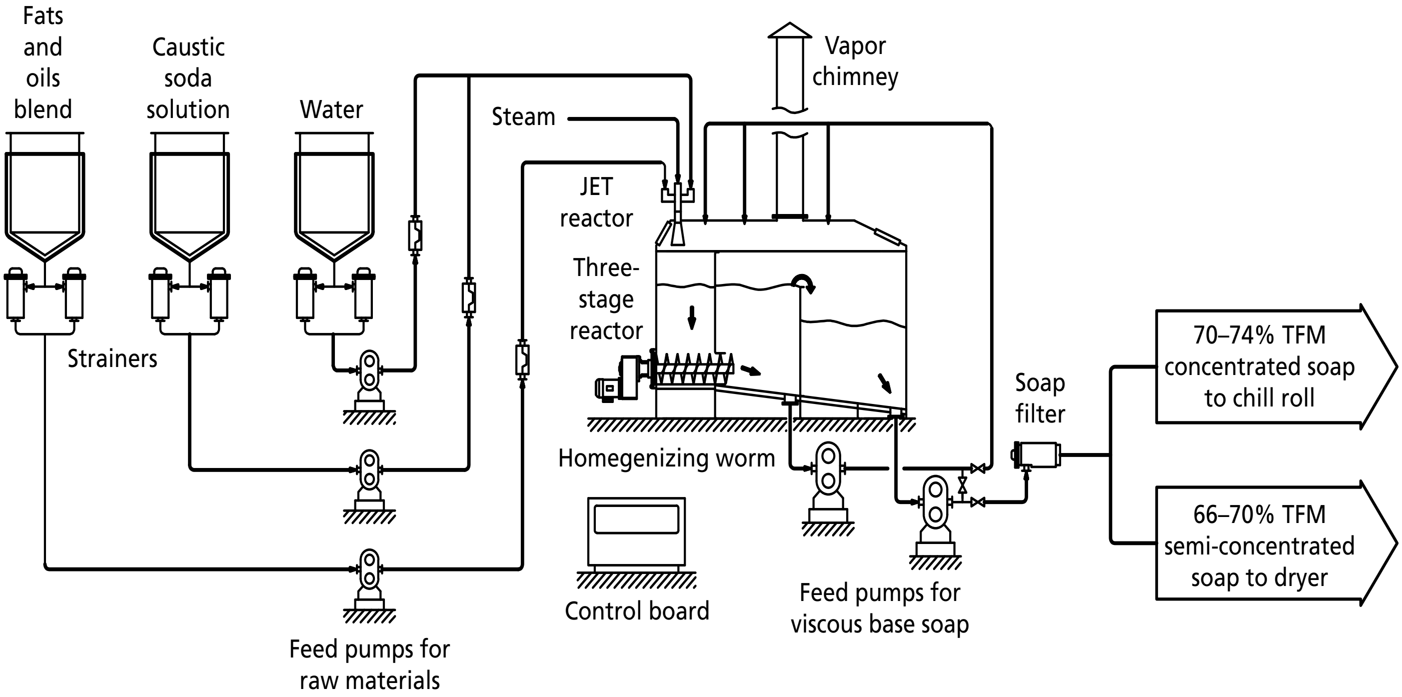

Figure 6.9 SAS saponification plant with JET reactor and 3-stage reactor.

Source: SAS.

SAS Saponification Plant with JET and Three-Stage Reactors

All the raw materials and steam are fed into the JET reactor, which feeds the formed emulsion into the first stage of the atmospheric three-stage reactor. A mechanical homogenizing screw feeds the second stage. The three-stage reactor completes the saponification in the second and third stages while the mass is mixed with a homogenizing worm and live steam. If more homogenization is needed, the soap can be recycled (Figure 6.10). The finished base soap is fed from the bottom of the third stage, and cooled down on a chill roll or dried on a vacuum spray dryer.

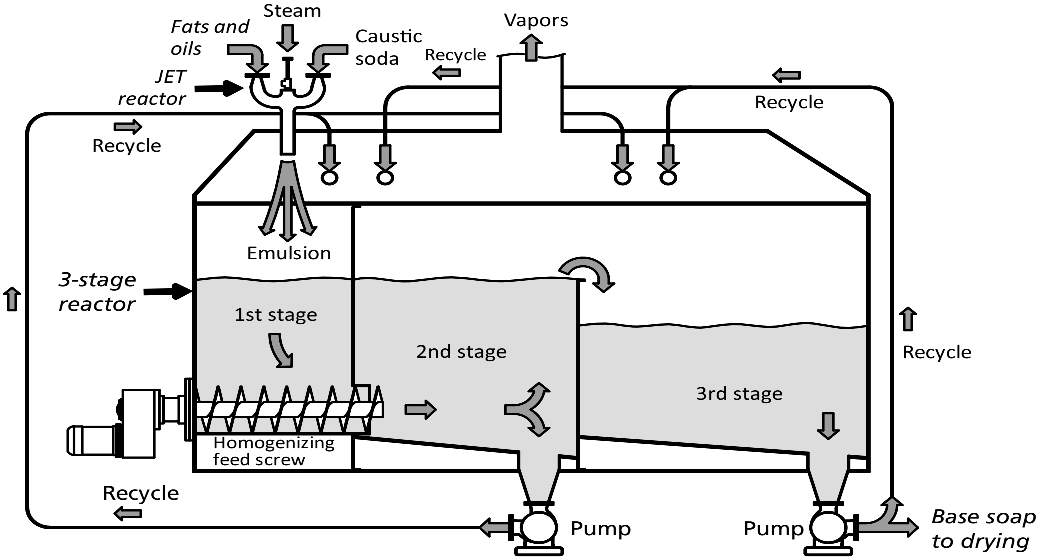

Figure 6.10 SAS JET and three-stage saponification reactors.
Source: SAS

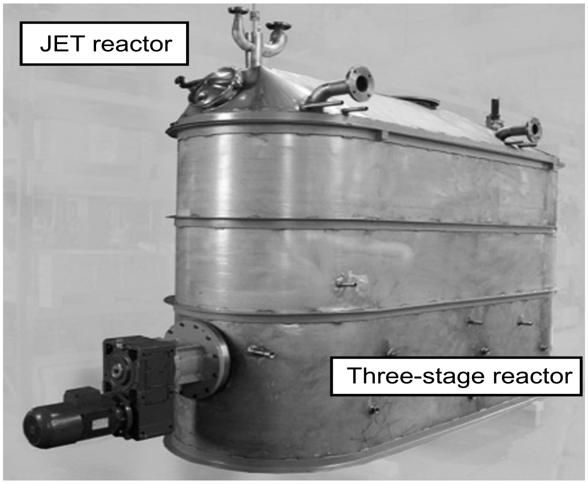

Figure 6.11 SAS JET and three-stage saponification reactors.
Source: SAS

SAS JET Reactor

The JET reactor initiates the saponification reaction between a small volume of fats and oils, caustic soap, and steam (Figure 6.12). The advantages of using a JET reactor are: reduction of saponification time, steam usage, and process water for production of standard, semi-concentrated, and concentrated base soaps. The JET reactor is easy to apply to all soapmaking systems

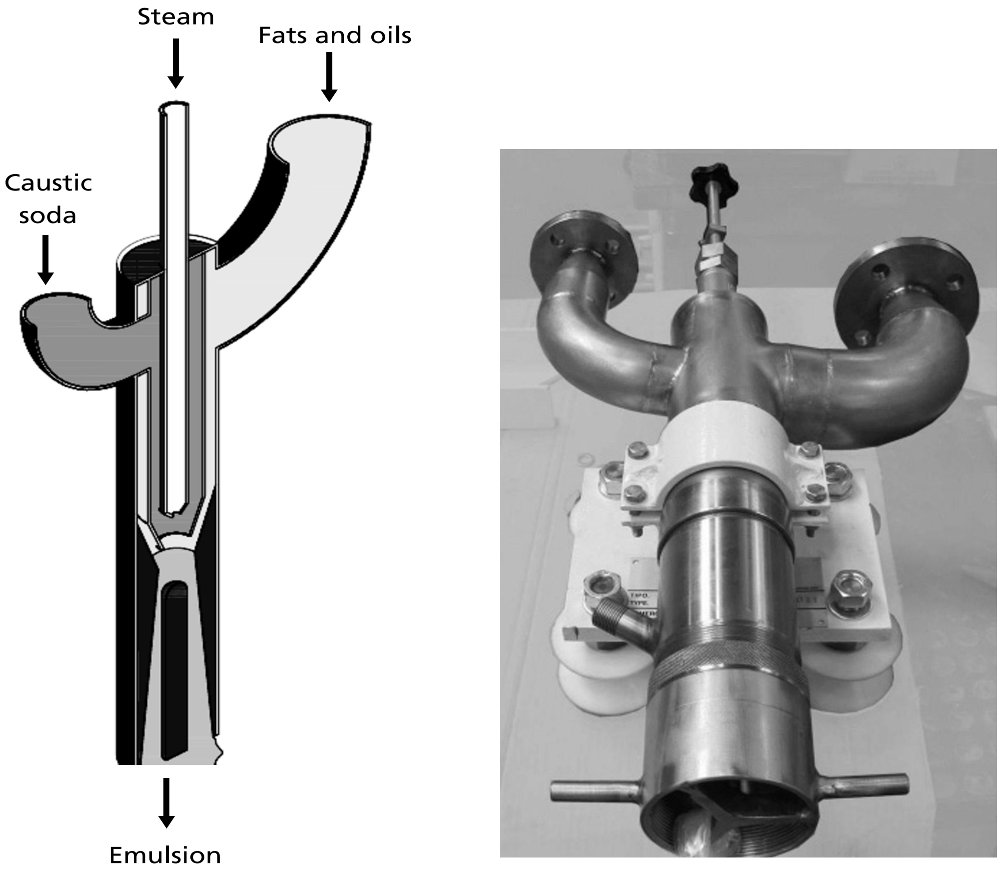

Figure 6.12 SAS JET reactor.
Source: SAS.

Soaptec Integrated Saponification and Drying Plant

Filtered raw materials are dosed in correct proportions into the reactor. Oils are kept at temperature in storage tanks, and caustic soda heats up during dilution with process water inside static mixers. Heat exchangers are provided to control the temperature of the fats and oils and caustic soda and the rest of the raw material. Minor ingredients are dosed at room temperature.

The reactor is divided into four sections with specially designed baffles fed with all the materials. Soap is formed quickly. Reaction is induced by the fact that the relatively small quantity of raw materials is injected into the stream of already-formed soap. A recycle loop ensures vigorous flow and good homogenization of all the ingredients.

The base soap (neat soap), using the reactor's pressure, goes to the spray chamber of the vacuum spray drying section of the plant. Moisture is removed from the base soap in pellet form and is extruded from a twin-worm plodder.

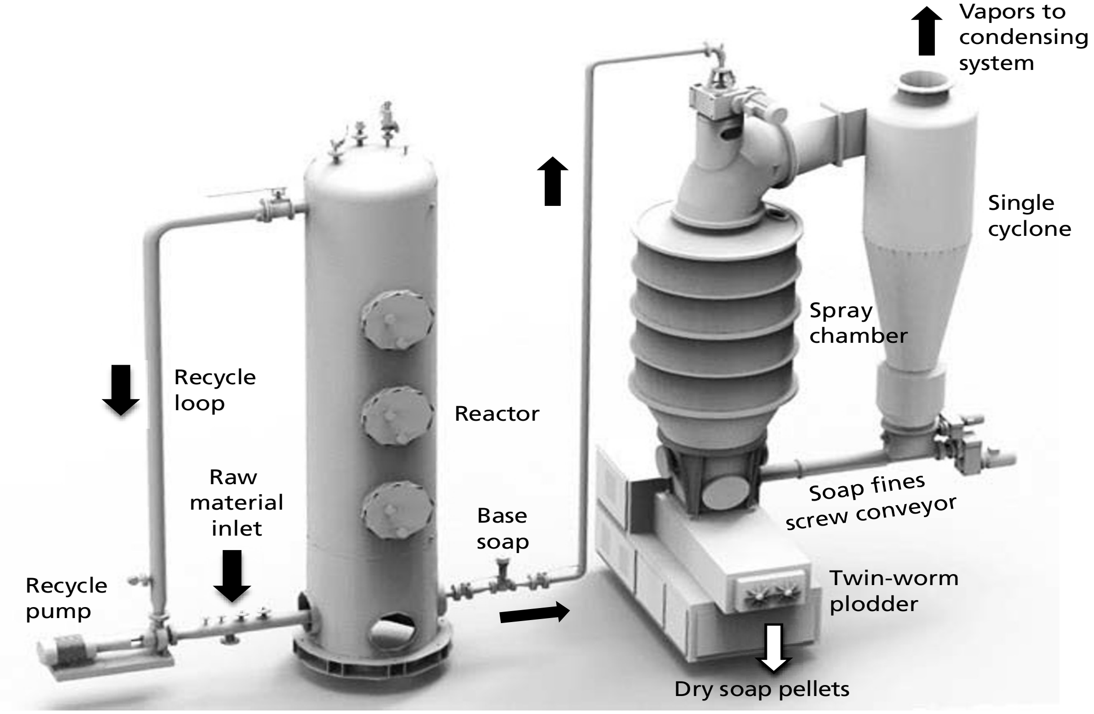

Figure 6.13 Soaptec integrated plant.
Source: Courtesy of Soaptec Srl.

Soaptec Reactor

The Soaptec reactor is divided into four sections with specially designed internal baffles for vigorous mixing of all of the ingredients. A recycle pump assists homogenization and completes the saponification of all types of fats and oils blends over a temperature range from 90 to 140 °C. The reactor has no moving parts.

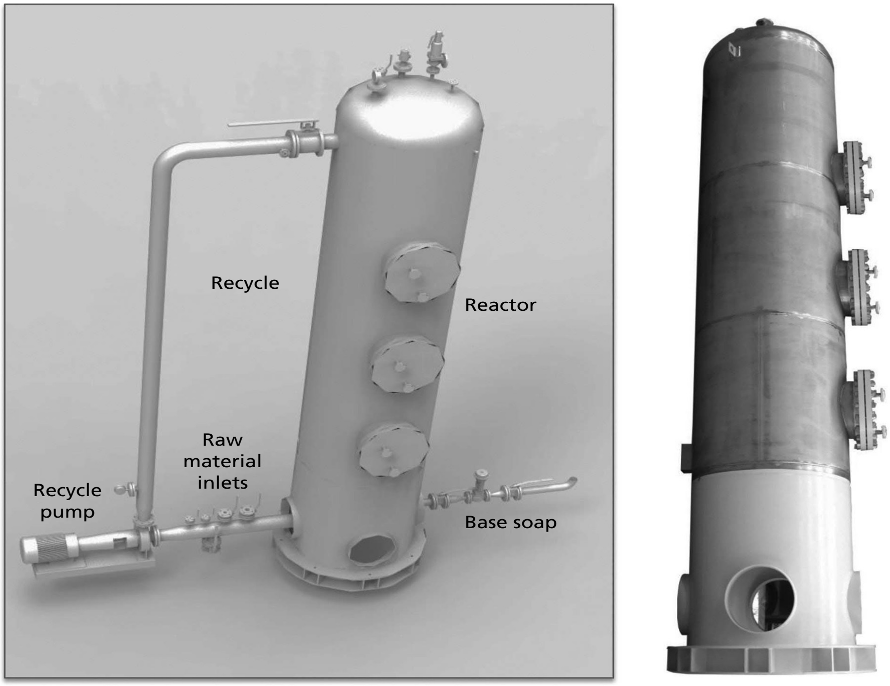

Figure 6.14 Soaptec reactor.
Source: Courtesy of Soaptec Srl.

Semi-Boiled Saponification Plant with Crutchers

Figure 6.15 illustrates a system with two saponification crutchers operating in tandem and an optional post-addition crutcher for minor liquid and solid additives. When the first one is fed with the raw materials, the second completes the saponification and discharges the semi-boiled SWING soap in a post-addition crutcher for final formulation with liquid and/or solid ingredients. The formulated base soap is ready to be dried. Plants with only one or two crutchers are available for producing economical soaps.

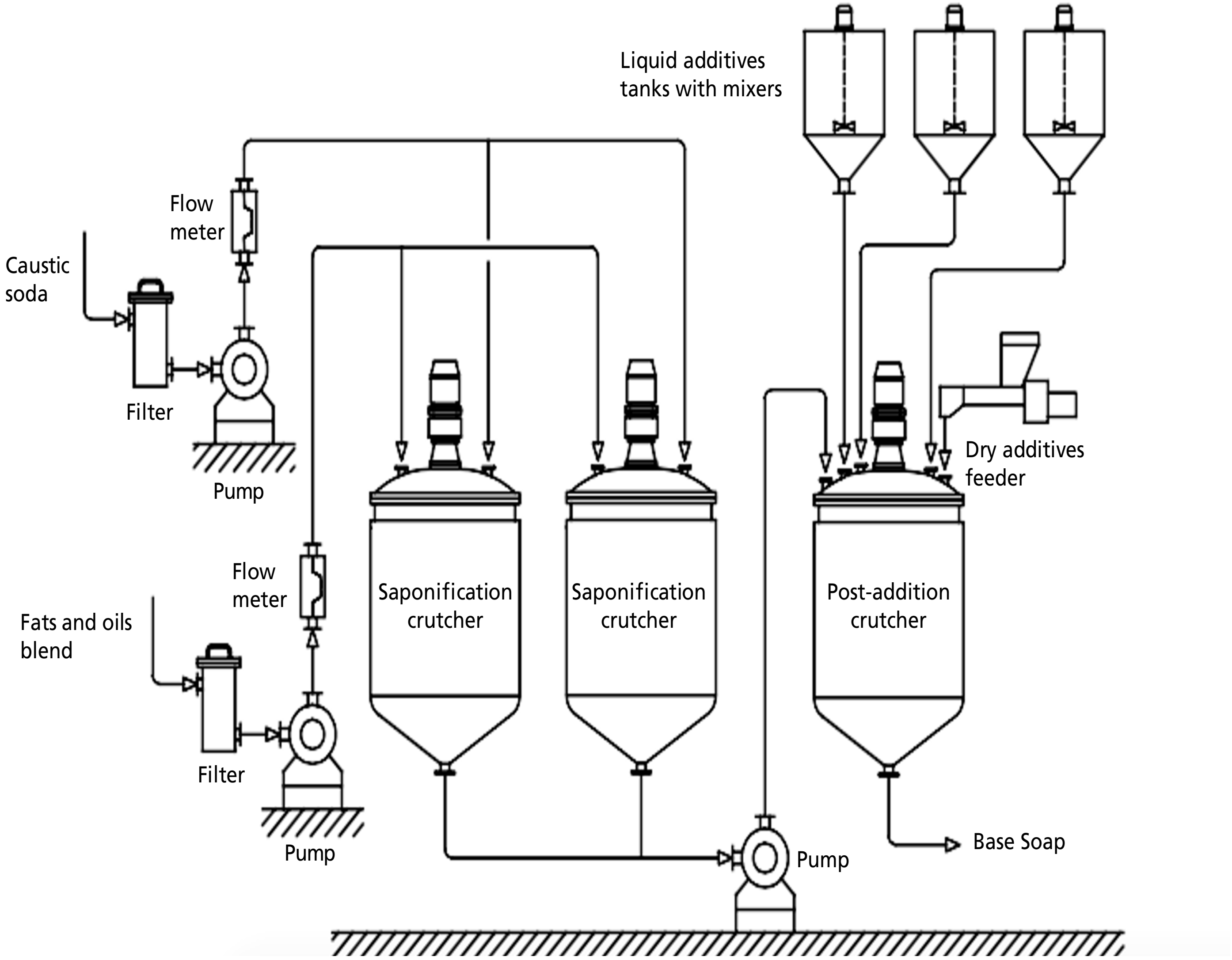

Figure 6.15 Semi-boiled saponification plant with three crutchers.

Source: SAS.

Crutchers

Crutchers are powerful, versatile mixers used for saponification of all types of raw materials (Figure 6.16). They are also used to incorporate liquid and solid additives into the soap. The key component of a crutcher is a vertical helical screw rotating inside a draft tube. The screw moves the product up inside the tube and moves it down outside the tube, providing vigorous mixing. Crutchers can operate under atmospheric or low pressure conditions.

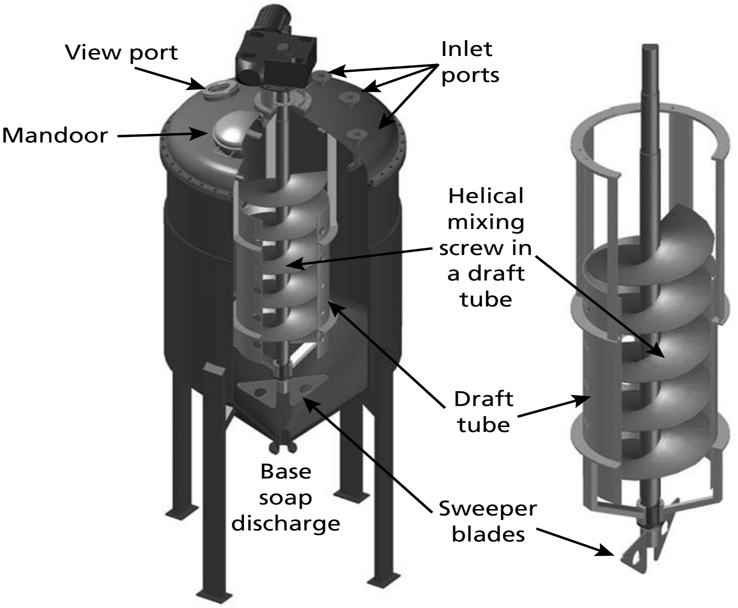

Figure 6.16 Crutcher.
Source: Soaptec Srl.

Acknowledgments

I appreciate the information and illustrations provided by Binacchi & Co., Mazzoni LB, SAS, and Soaptec Srl. Their assistance made this chapter possible.

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7 Soap Drying Systems

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Soap Drying Systems

Drying is a very important processing step in soap manufacturing. The drying system used affects the physical properties of the dried soap (details are given in Chapter 2). Optimum final moisture content of the soap pellets (noodles), temperature, and physical characteristics are critical variables for obtaining the best finished bar performance and finishing line productivity.

Liquid base soap (neat soap) with water content ranging from 22–31% (coming directly from a saponification reactor) or 29–34% (neat soap from a storage tank), can be dried to different moisture content (MC) ranges:

- Toilet soap pellets (noodles): normally 12–15% MC, exceptionally as low as 10%
- Special soap pellets (translucent or multipurpose): 16–22% MC
- Laundry soap pellets/bars: 22–30% MC

Vacuum Spray Drying

Vacuum spray drying, patented by Giuseppe Mazzoni, was introduced for industrial applications following World War II. The use of vacuum as a medium to simultaneously dry and cool the liquid neat soap is responsible for the beginning of the modernization of soap manufacturing.

Plants using this system were designed to convert liquid neat soap into dry toilet soap pellets and could also be equipped to produce continuously extruded laundry soap bars. The elimination of the laborious and costly laundry soap framing process used until the advent of power detergents was a revolutionary step in soap manufacturing.

Vacuum spray drying is still is the most widely used process for toilet and laundry soap applications. It is a very flexible and simple-to-operate system for the production of various types of soaps at different moisture levels.

Other Drying Systems

Hot-Air Cabinet Dryers

Before the invention of vacuum spray drying, hot-air cabinet dryers were used. Neat soap was fed onto a steam-heated chill roll and then onto a steel belt of a long and large cabinet in which hot air completed the drying of the soap in flake form.

Hot-Air Spray Towers

In a few factories, hot-air spraying towers similar to detergent-production plants are used for soap drying, but application of this type of system is limited by high energy requirements, large space requirements, and, last but not least, the high temperature and the physical characteristics of the dry soap obtained this way.

Expansion Dryers

After the Mazzoni vacuum spray drying process, only a few soap drying systems were introduced. The tubular drying system appeared in 1955, and the Parkson atmospheric dryer with a plate evaporator and a chill roll appeared in 1966 (Palmason, 1963). Alfa-Laval also offered a similar system. Only a few of these dryers were installed.

In 1960, Miag developed, in collaboration with the 4711 soap factory in Cologne, Germany, a "double expansion drying" system and patented it in 1964 (Miag GmbH, 1964). The tubular, plate, and double expansion dryers did not gain acceptance.

Toilet and Laundry Soap Vacuum Spray Dryers

During recent years, most of the effort to optimize vacuum spray drying plants has focused on reducing energy requirements, improving pollution control, and the design of large industrial units capable of processing soap pellets or laundry bars at up to 15 tons/h. Figures 7.1 and 7.2 show the current Mazzoni LB design for toilet and laundry soap drying.

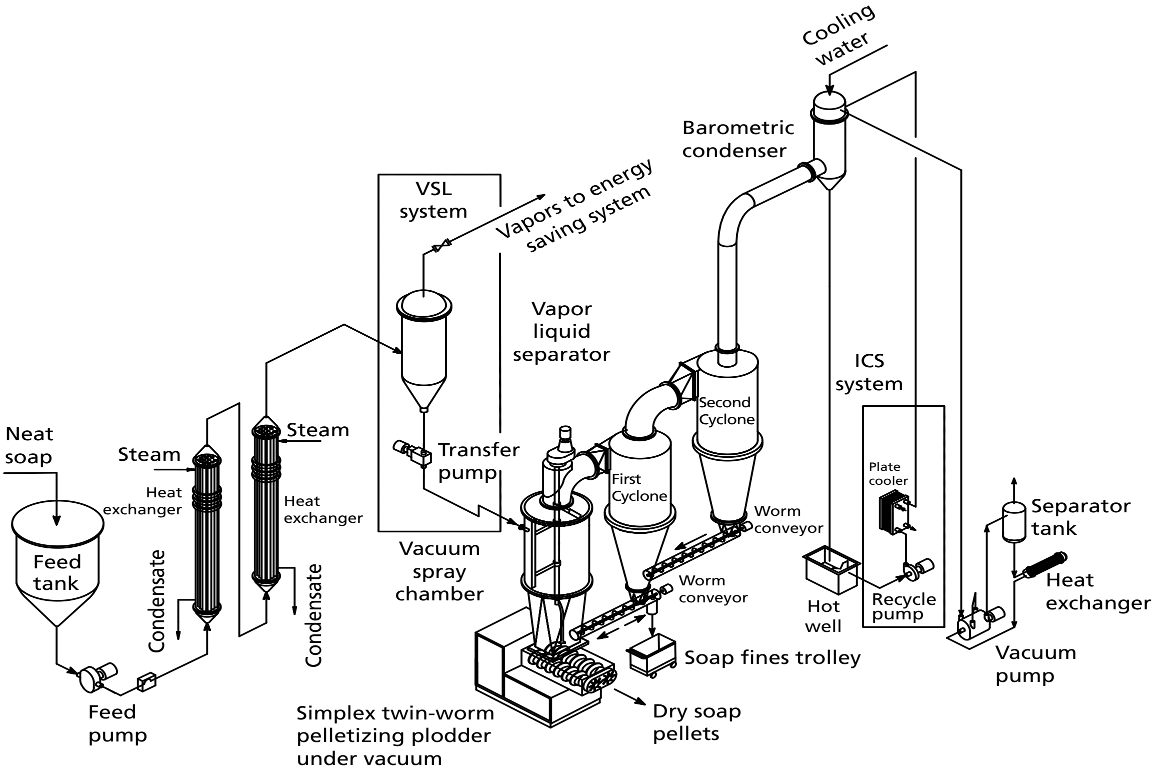


Figure 7.1 Mazzoni LB "ecodryer" toilet soap vacuum dryer with vapor liquid separator (VLS).

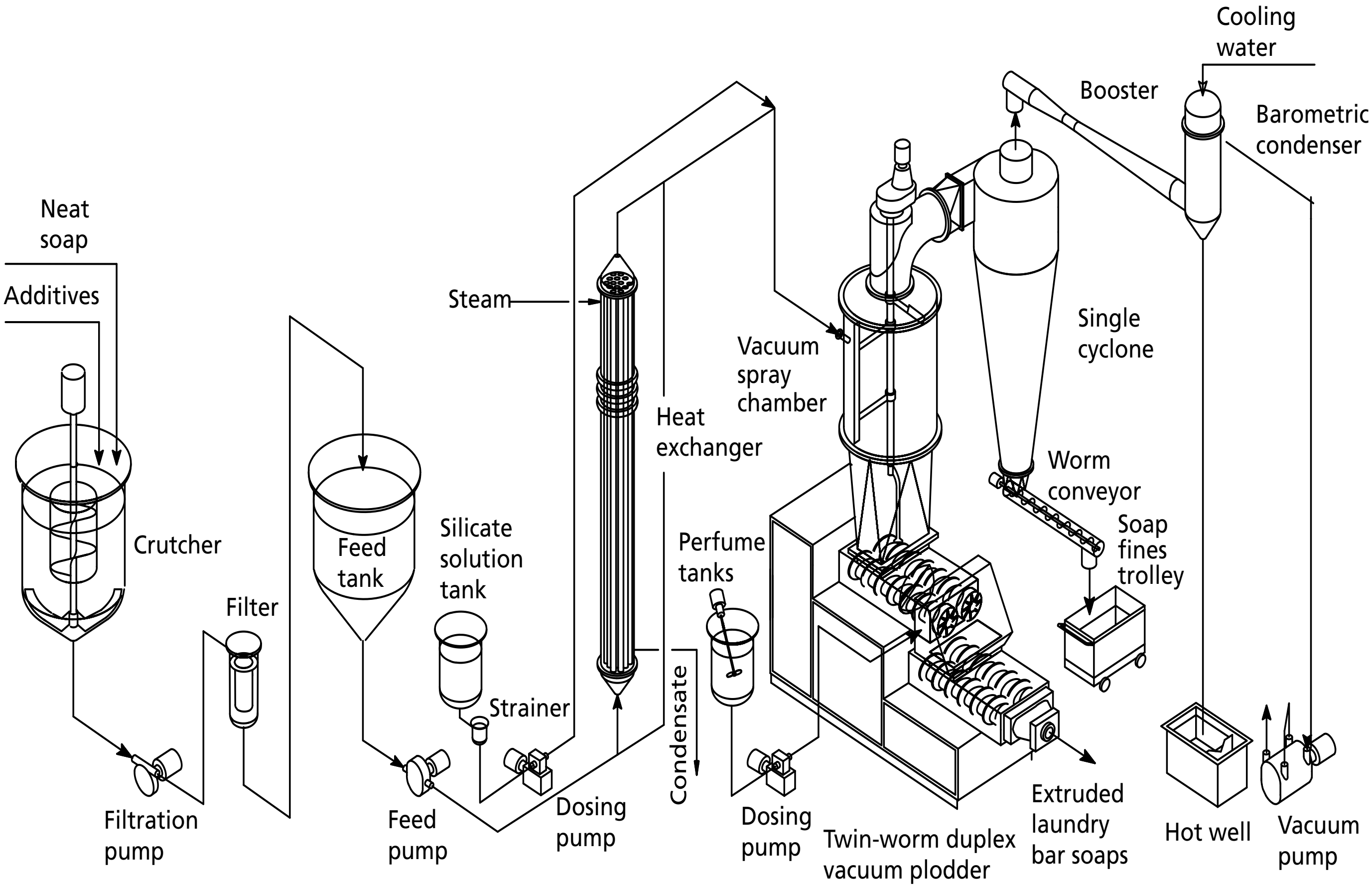


Figure 7.2 Laundry soap vacuum spray dryer.

The most important new developments are the “integrated” plants, which consists of a continuous saponification/neutralization unit in combination with a vacuum dryer for the direct processing of the neat soap into dry pellets. In these compact plants there is no need for any storage tanks in between the two units. This design is shown in Chapter 6 of this book.

Process Flow Diagram

Toilet Soap Dryers

The following table compares the processing steps for a traditional toilet soap dryer and the new, updated systems in current use.

Operating Step	Traditional	Current	Integrated Plant (Standard Concentration Reactors)	Integrated Plant (High Concentration Reactors)
1	Neat soap feeding	Neat soap feeding	Neat soap from the reactor	Neat soap from the reactor
2	Preheating and pre-evaporation	Preheating and pre-evaporation	Preheating and pre-evaporation	—
3	—	Vapor separation	—	—
4	Vacuum drying	Vacuum drying	Vacuum spray drying	Vacuum spray drying

Current Stand-Alone Dryers

For Step 3 a vapor–liquid separator or vapor eliminator (VLS) is used. Step 4 can be done in a conventional vacuum chamber (atomizer) with a rotating nozzle and scrapers, or in the new Mazzoni LB vacuum chamber with a stationary inlet nozzle (no spray vacuum chamber).

The main advantages of using a VLS system are as follows:

- Increased production capacity
- Utilities savings and energy recovery options
- Reduced quantity of soap fines
- Improved vacuum level

The key processing variables that affect and control vacuum spray drying of liquid toilet soaps and laundry soaps are illustrated in detail in Figure 7.3 for 78–80% TFM toilet soap drying. Figure 7.3 explains also the drying process for integrated plants:

- For high concentration integrated plants, that is, when soap from the reactor has about 22–24% moisture, soap is just expanded into the vacuum chamber (last zone on the right of the diagram).
- For standard concentration integrated plants, that is, when soap from the reactor has a moisture content of 28–29% or more, soap passes through the heat exchanger for water pre-evaporation (central zone of the diagram) and then is expanded into the vacuum chamber (last zone on the right of the diagram).

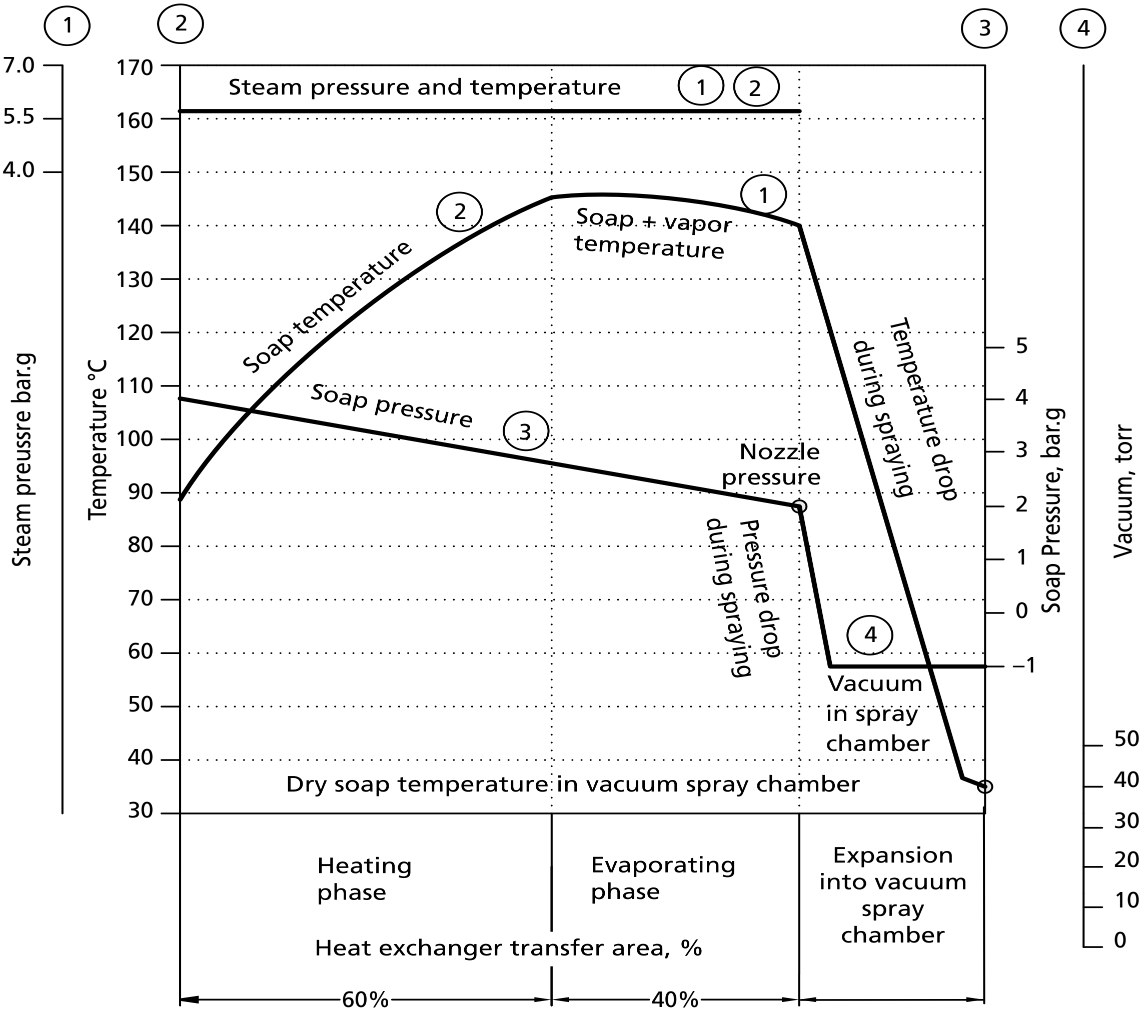


Figure 7.3 Drying system for 78–80% TFM laundry soaps.

The variables shown are steam pressure, soap pressure and temperature, spray nozzle pressure, operating vacuum, and dry soap temperature leaving the system. The heating and evaporating phase distribution is also shown.

The function of toilet soap vacuum spray dryers is to convert liquid neat soap into dry soap pellets (noodles) by removing moisture. To evaporate the necessary amount of water to reach the desired final moisture, the neat soap/water mixture has to be heated to its boiling point. Vacuum is used as a medium to obtain soap drying and cooling simultaneously.

Standard, superfatted, and translucent bases with different moisture levels can be produced with ease by simply changing operating conditions. The preheated soap and vapor mixture coming from the heat exchanger is normally first sent to a VLS, which consists of a static vessel where pre-evaporated water vapor is separated by gravity from hot liquid soap under controlled temperature and pressure.

The normal operating pressure for the VLS is 1.4–1.7 bar, which is also the optimal back pressure for the heat exchanger operation and the vapor-liquid separation. The vapors from the VLS can be used for various energy conservation purposes, as discussed separately. The soap from the bottom of the VLS is pumped under level or flow control to a vacuum chamber. There are two types:

1. *Rotating spray nozzle (conventional design).* This is equipped with rotating scrapers and a spray nozzle assembly.
2. *Stationary inlet nozzle ("no-spray").* This new Mazzoni LB vacuum chamber is equipped with a tangential stationary soap inlet nozzle, rotating scraper, and anti-entrainment internal baffle.

As the vapors are flashed off because of the vacuum, the soap dries to its final moisture. The rotating scrapers remove the dried and cooled soap, in flake form, from the chamber walls. The unevenly shaped dry soap flakes fall onto plodders to be pelletized.

During spraying, a certain amount of soap fines are formed and are carried off with the high-velocity vapors into cyclone-type fines recovery systems before being condensed in a condenser. A vacuum pump, steam ejector, or a combination of the two maintains the vacuum and removes the noncondensables.

Integrated Dryers

The integrated dryers receive the base soap directly from a saponification/neutralization reactor without passing through an intermediate storage tank; therefore, all the heat contained in the mass coming from the reactor is used for drying the soap base.

The configuration of the integrated dryer depends mainly on the moisture contained in the base soap coming from the reactor and on the desired final product.

When the moisture of the base soap is 29–31% (standard concentration reactors), a shell and tube heat exchanger is used between the reactor and the dryer for toilet soap pellet production. The heat exchanger will pre-evaporate the necessary amount of water to reach the final soap pellet moisture.

The surface area required for the heat exchanger is approximately 50% of that of a stand-alone dryer since the heat of reaction is not lost but is used for drying. For laundry soap production, the heat exchanger can be omitted in most cases.

When the moisture of base soap is 22–24% (high concentration reactors), the soap is fed from the reactor to the vacuum chamber. Final moisture content is adjusted, regulating the moisture in the reactor.

In the latter case, due to the reduced amount of vapors released under vacuum, dust generation and cooling water requirements for the barometric condensers are drastically reduced when compared to a stand-alone dryer.

Laundry Soap Dryers

Fewer innovations have been applied to laundry soap dryer designs compared to toilet soap dryers. The VLS system cannot be employed for laundry soaps because there is little or no pre-evaporation of water before the vacuum chamber. The processing steps for laundry soap dryers are as follows:

	Conventional Laundry Soap Dryers			Integrated Laundry Soap Dryers		
Operating Step	**Pure Laundry Soap**	**Filled Laundry Soap with Solid Fillers**	**Filled Laundry Soap with Liquid Fillers**	**Pure Laundry Soap**	**Filled Laundry Soap with Solid Fillers**	**Filled Laundry Soap with Liquid Fillers**
1	Crutching (solids mixing and/or other additives)			—		
2	Neat soap feeding			Neat soap from the reactor		
3	Preheating only for higher than 68% TFM soaps	—	Preheating only for higher than 68% TFM soaps	—		
4	—	Liquid filler injection (if applicable)	Liquid filler injection	—	Liquid filler injection (if applicable)	Solid additives injected as water slurry or premixed with oil before saponification
5	Vacuum spray drying			Vacuum spray drying		
6	Extruding finished laundry bars or pelletized laundry soap base			Extruding finished laundry bars or pelletized laundry soap base		

Perfume and color are added by dosing systems in the plodders, where the soap is already compact, in order to minimize perfume losses in the vacuum.

The principles of vacuum spray drying of the various types of laundry soap products into a dry base in bar form at various moisture levels are shown in Figure 7.4 for 68–70% TFM laundry soaps and in Figure 7.5 (p. 141) for lower than 68% TFM laundry soaps.

Figures 7.4 and 7.5 also explain the drying process in case of integrated plants. For laundry soap production, soap from the integrated reactor is just expanded into the vacuum chamber (last zone on the right of the diagrams). The moisture content and the temperature of soap from the reactor can be adjusted based on final product desired, as explained below.

The figures show how the vacuum spray drying process is affected and controlled by key variables, such as steam and soap pressure and temperature, spray nozzle pressure, operating vacuum, dry soap temperature leaving the system, and the heating and evaporating phase distribution.

The function of laundry soap vacuum spray dryers is to convert liquid neat soap into dry soap bars with various additives and fillers by removing moisture. Vacuum is used to obtain soap drying and cooling simultaneously. Pure unfilled, filled, and other types of bars of different moisture levels can be produced with ease by simply changing the operating conditions.

Preheating is required only to produce soap bars with higher than 68% TFM content, starting from a regular 62% TFM neat soap. Simple flashing-off under vacuum drying

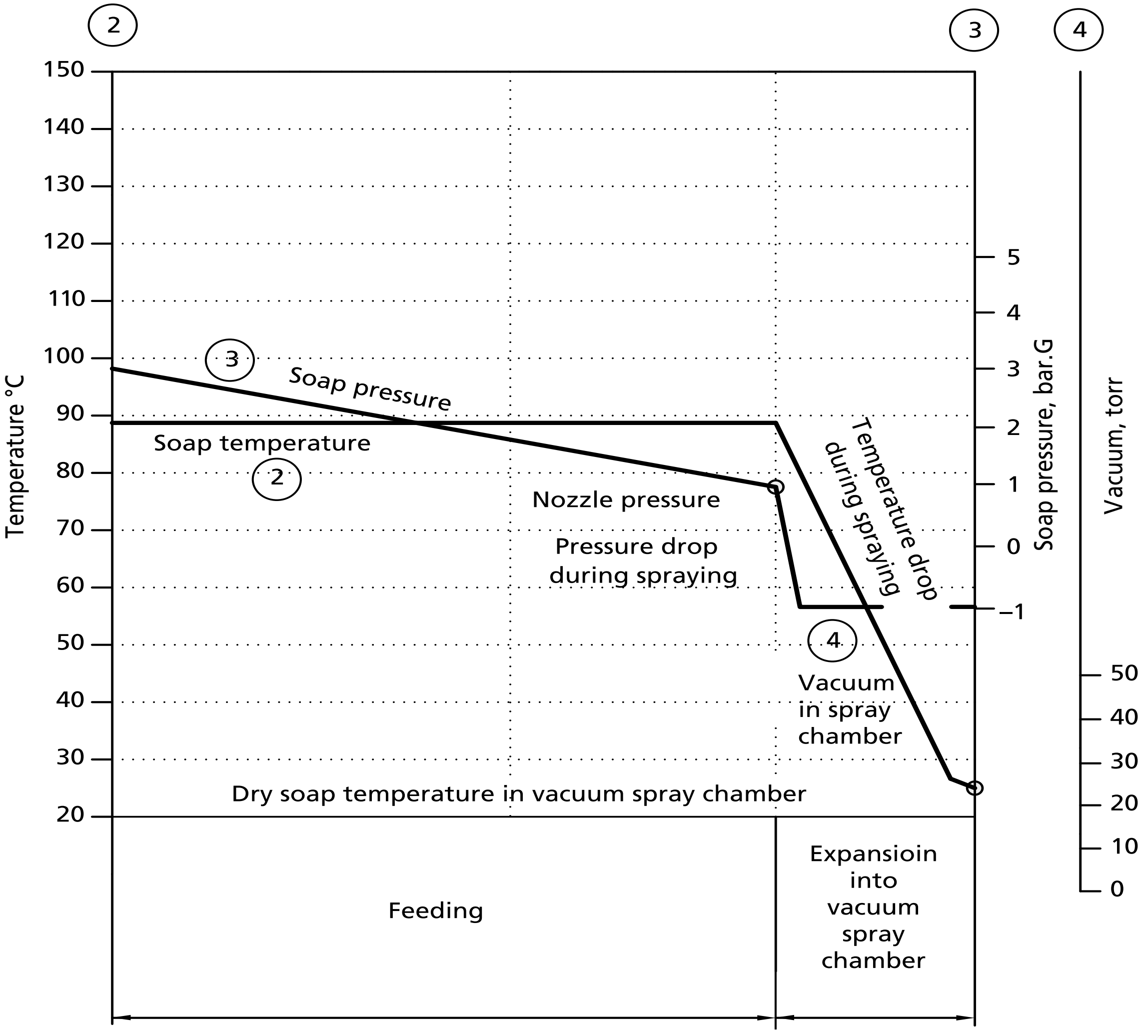


Figure 7.4 Drying system for less than 68–70% TFM laundry soaps.

without any preheating allows a final product with 67–68% TFM content to be reached. In any case, the heat exchangers are used only to increase the soap temperature without pre-evaporating water; this makes the application of the VLS useless for laundry soap dryers.

If preheating is needed for liquid fillers, an inline mixer must be used after the heat exchanger. The preheated soap is directly sent to the vacuum chamber, which can be of the same type used for toilet soaps.

In case of integrated plants, there are two different options:

1. Neat soap from tubular reactors, coming at 120–130 °C.
2. Neat soap from continuous crutcher type reactors at 95 °C or higher temperature. In this case, the same principles as for a conventional stand-alone dryer can be applied.

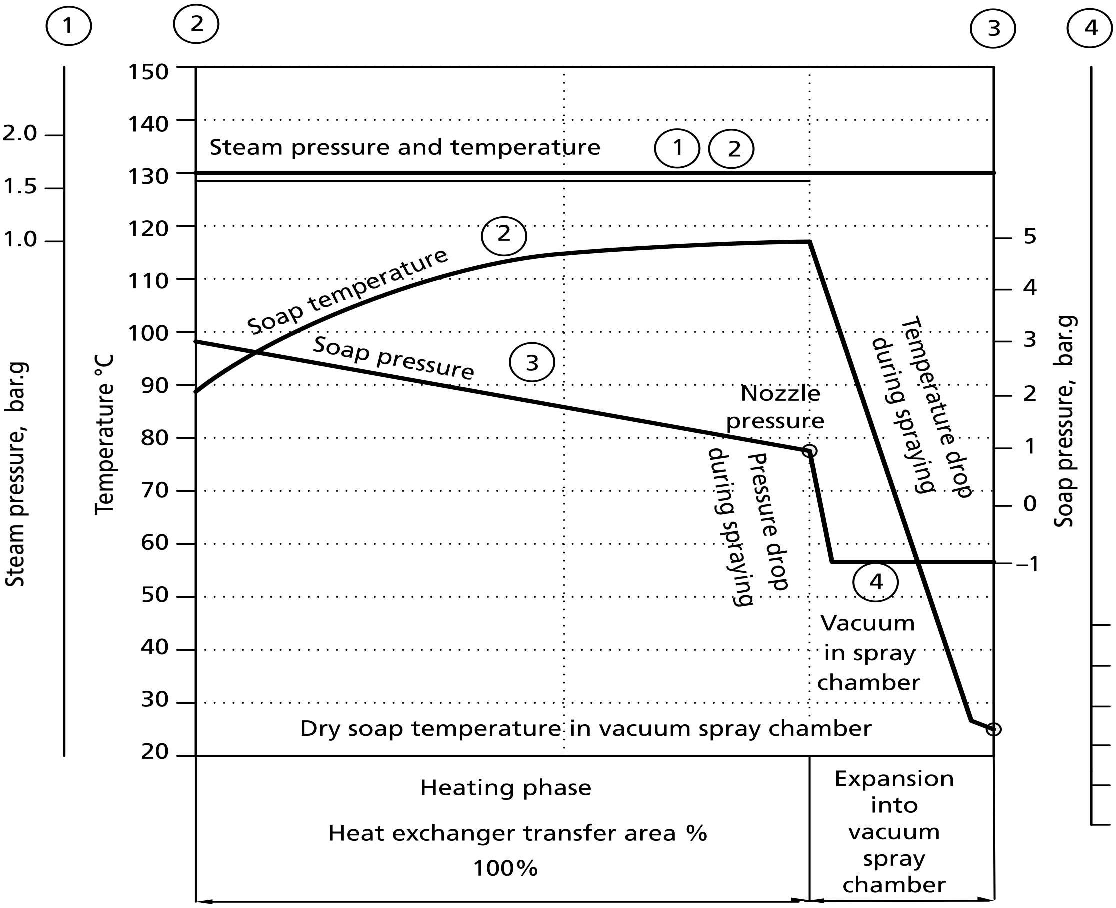


Figure 7.5 Drying system for 68% TFM laundry soaps.

As the vapors are flashed off because of the vacuum, the soap dries to its final moisture. The rotating scrapers remove the dried and cooled soap, in flake form, from the chamber walls. The unevenly shaped dry soap flakes fall onto a duplex plodder to be pelletized in the first stage plodder and then extruded in the form of a continuous slug (billet) from the second (last) stage plodder. The extruded slug can be directly engraved, cut, and packed, or directly sent to a laundry soap finishing line that has a soap press. Laundry soap pellets can also be produced for sale.

During spraying, a small amount of soap fines are formed, which are carried off with the high-velocity vapors into cyclone-type fines recovery systems before being condensed in a condenser. A vacuum pump, steam ejector, or combination of the two maintains the vacuum and removes the noncondensables.

Table 7.1 Typical Spray Dried Soap Products and Operating Data

	Toilet Soap Base Pellets (Noodles)		Translucent Soap Pellets/Bars	Laundry Soap Bars			
	Standard	**Superfatted**	**Translucent**	**Opaque Pure**		**Opaque Filled**	
Product Characteristics							
Total fatty matter content, % TFM	Normal range 78–80 Wide range 78–84	80–84	68–72	68–72	62–63	55	45–50
Moisture content, %H_2O	Normal range 13–15 Wide range 14–8	12–10	18–22	25– 21	32–31	32–28	32–28
Operating Conditions							
Heat exchanger steam pressure, bar.g	5–6		0.5–1.5	0–2	Not Used	Not used	Not used
Soap temperature after heat exchanger, °C	130–140		105–115	110–115	85–90	85–90	85–90
Pressure in vapor liquid separator, bar.g	1.3–1.7		Not used	Not used	Not used	Not used	Not used
Absolute pressure in vacuum chamber, torr	30–50		20–30	20–25	15–20	10–15	10–15
Plodder selection guide	One or two single-worm plodder ***or*** one or two twin-worm plodder(s)		Two single or twin-worm plodders with a vacuum chamber at the final extrusion stage	Two single or twin-worm plodders with a vacuum chamber at the final extrusion stage		Two or three twin-worm plodders with a vacuum chamber at the final extrusion stage	

Dryer Operating Data for Toilet Soap Pellets and Laundry Soap Bars

The operating parameters for the vacuum spray dried production of the most typical dried toilet soap bases in pellet form and laundry soaps in bar form are summarized in Table 7.1. A suggested plodder selection guide is also listed.

Dryer Equipment and Components

Filtration Pumps and Filters

Continuous saponification plants produce clean neat soap, whereas soap made via a kettle, or a semiboiled process in a crutcher, can contain impurities. Filters protect the feed pump, the heat exchanger, and the spray nozzles from damage due to foreign bodies.

Hollow disc type filtration pumps can handle impurities and still provide sufficient pressures of 3–4 bar to send soap to the dryer feed tank.

A complete filtration section with pump, dual filters, and an automatic control system is illustrated in Figure 7.6. Basket filters with drilled steel-plate filtering equipment, with or without screens, are used in horizontal or vertical position.

Typical filtering elements are as follows:

- For toilet soap: drilled plate with 2 mm diameter holes, covered with 30–50 wire mesh screen

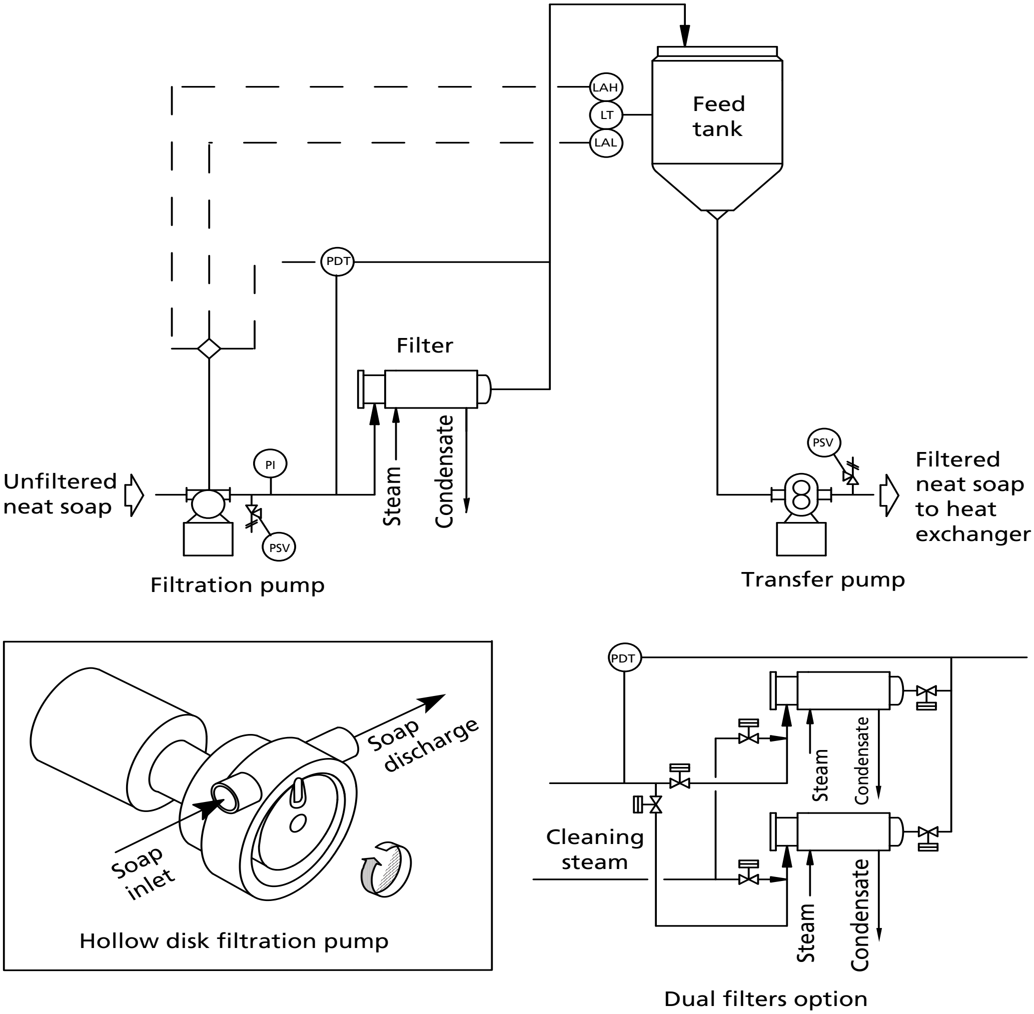


Figure 7.6 Filtering section: Filtration pump and filters automatic control.

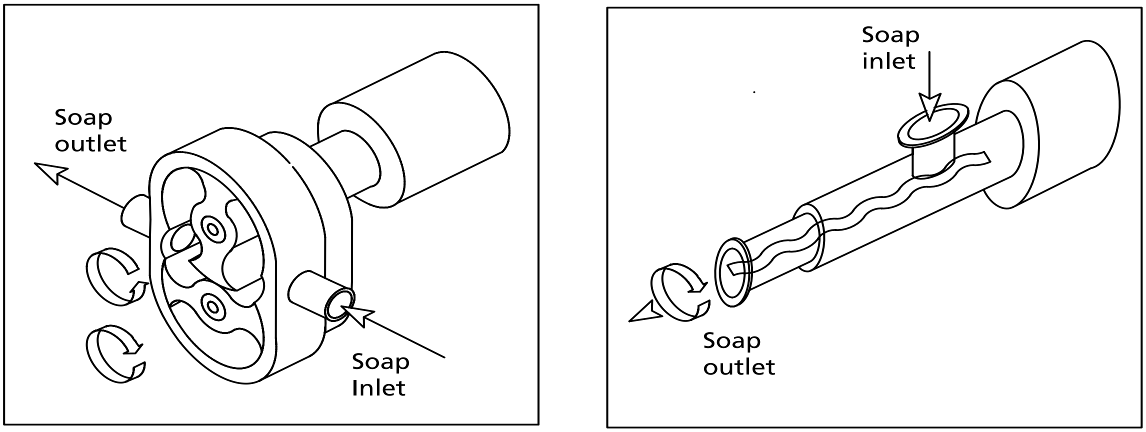
- For laundry soap: drilled plates with 0.5–0.8 mm holes
- A fast changeover filter is installed for continuous operations. Filter clogging is detected by a differential pressure transmitter, and the signal is used to stop the filtration pump or to switch over to the clean second filter. The use of bag filters is recommended when polyethylene contamination from fats packaging occurs.

Feed Pumps

The most widely used soap feed pumps are shown in Figure 7.7. External and internal gear pumps provide excellent positive flow with nonpulsating discharge. Internal gear pumps offer the advantage of having only a single shaft and one mechanical seal or stuffing box. External gear pumps can be made with spur, helical, or fishbone gears.

Lobe Pumps
Bi-Lobe and Tri-Lobe

Mono Screw Pump



Internal Gear Pump

External Gear Pump

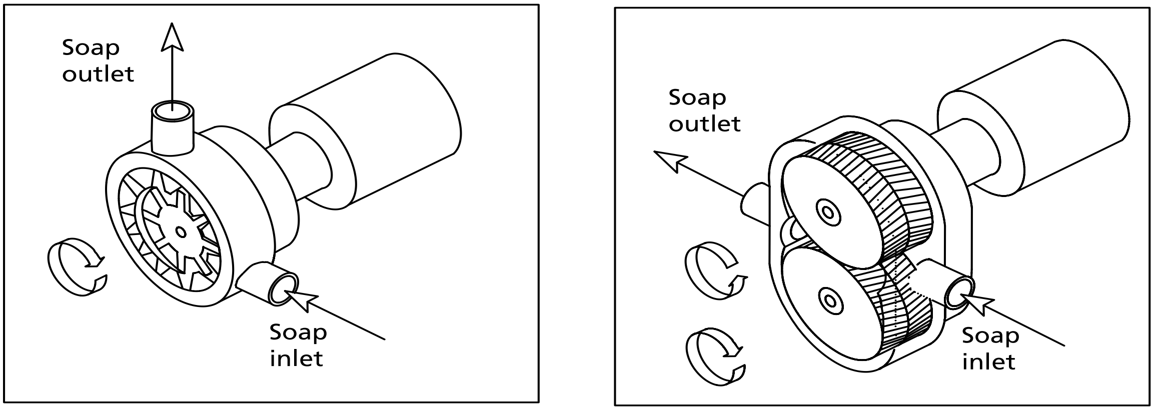


Figure 7.7 Feed pumps.

Lobe pumps, today the most widely used, are also excellent for pumping shear-sensitive fluids such as neat soap. They are available in bi-lobe or tri-lobe designs. A particular feature of lobe pumps is that the rotors and seals can be accessed easily by removing the font cover, without disconnecting the process line. It is suggested to limit the rotating velocity to 200 rpm in order to select a pump with sufficiently large inlet pipe sizes to allow easy pump feeding.

Mono screw pumps also provide excellent flow and pressure stability, but their application is limited due to wearing of synthetic material stators with consequently high maintenance costs. To extend the life of these pumps, they are selected with very low rotation speed, such as 50 rpm maximum. They can be a good choice when abrasive components are added to neat soap. Whereas a lobe pump would suffer due to lobe abrasion, for the mono pump, the stator is the sacrificial element that preserves the stainless steel casing and worm.

Heat Exchangers

Shell-and-Tube Heat Exchangers

Single-pass shell-and-tube heat exchangers for soap applications are simple in design. A number of straight tubes are sealed between two perforated tube sheets. The tube plates and cones are made of 304, 316, or 316L stainless steel. To avoid stress corrosion cracking problems with soap formulations containing higher than 0.6–0.7% salt content in the neat soap, high-nickel-content materials, such as Alloy 825 (Unified Numbering System UNS-N08825), are recommended. Expansion joints should be used to prevent mechanical stresses.

The optimum tube sizes used are 10 mm ID/12 mm ID or 12 mm ID/14 mm ID. Shell-and-tube exchangers have the lowest capital cost per square meter of heat transfer area and can be installed in various configurations:

- A single vertically placed heat exchanger for any plant capacity
- Two equally sized heat exchangers in series

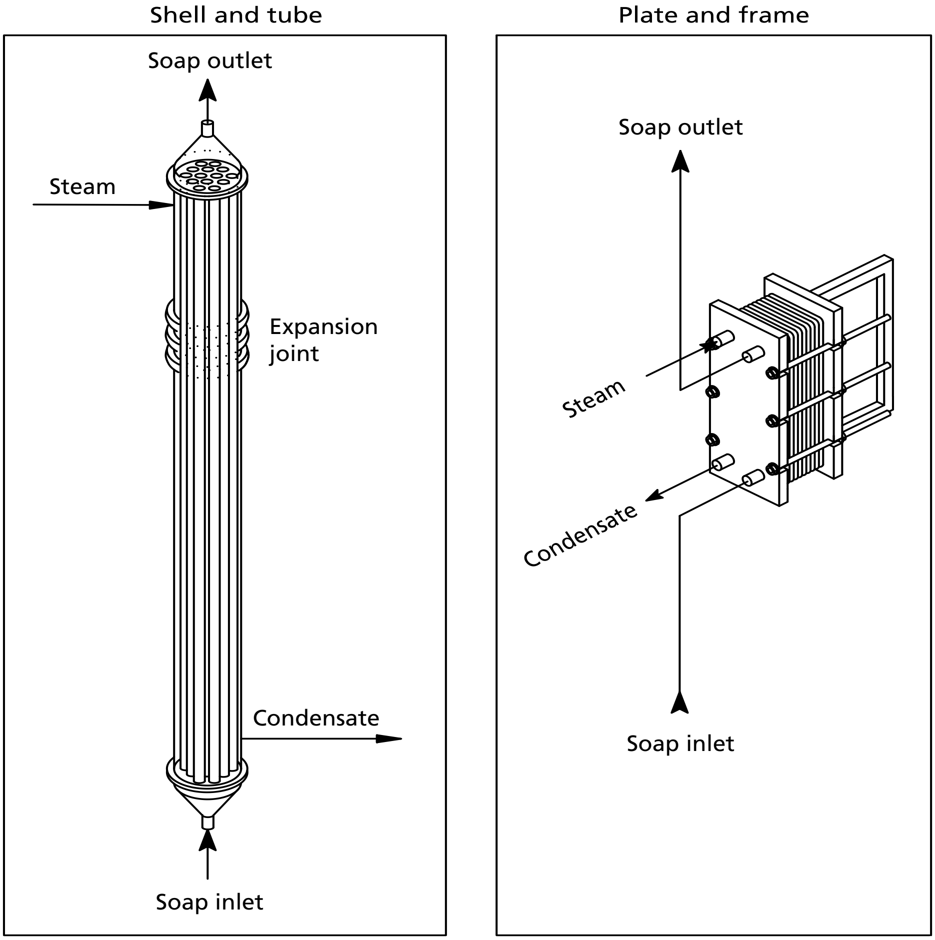


Figure 7.8 Heat exchangers.

Typical heat transfer surface areas for tube-and-shell heat exchangers used for vacuum spray dryers are, for toilet soap, 20–30 m^2/ton of dry soap, and, for laundry soap, 10–15 m^2/ton of dry soap. The actual selected area depends on the initial and final soap moistures of the processed soaps.

The 10/12 mm diameter tubes provide about 10–15% higher heat transfer rate than the 12/14 mm size tubes, so that when 12/14 mm tubes are used, the surface of the heat exchanger is higher. But the 12–14 mm tubes are more suitable to handle "semi-boiled soap" and soaps rich with additives, as they cause lower pressure drops.

Plate-and-Frame Heat Exchangers

Plate-and-frame heat exchangers (PAF) consist of a number of thin, corrugated metal plates and gaskets clamped together and fitted with a frame. The turbulence of the flowing material induced by the surface design of the plates results in a 3–5 times higher heat transfer coefficient *U* (see the Appendix to this chapter).

Previously, the use of PAF exchangers for soap drying was limited due to the gasket materials and their replacement costs. Today, the use of ethylene propylene diene monomer (EPDM) gaskets designed for 200 °C maximum temperature and 25 bar pressure has eliminated the problems encountered with less resistant gaskets.

Drying of high moisture content, heat sensitive soap/synthetic (combo) products requires high pre-evaporation rates in the atmospheric drying stage. For this application, PAFs provide homogeneous two-phase flow with a higher steam rate.

PAF heat exchangers cost more per square meter of heat transfer area than shell-and-tube units, but their high heat transfer rate, compact size, and use for special applications can make them cost-effective.

The higher maintenance cost of PAF exchangers compared to shell-and-tube exchangers has limited application of PAFs to the special cases just described.

Vapor–Liquid Separators

The first vapor-liquid separator (VLS) to be used with vacuum spray dryers was installed in 1987. It took many years for the soap industry to accept the use of this novel system. The VLS is positioned between the heat exchanger and the vacuum spray chamber, and it disengages the vapors formed in the heat exchanger before the soap-and-vapor mixture reaches the vacuum spray chamber.

Mazzoni LB VLS Design

The Mazzoni VLS unit consists of a vertical static vessel operating under a pressure of 1–2 bar, where the vapors that were formed in the heat exchanger separate from the liquid hot soap due to gravity.

The separation is governed by the pressure-controlled outlet of vapors from the top part and the level-controlled extraction of soap from the bottom. The pressure is maintained by a control-modulating valve on the vapor line, whereas the soap level is controlled by varying the speed of the pump under the VLS. This pump, which feeds the soap to the drying chamber, is a lobe or gear pump, preferably vertically mounted so that soap can directly fall into the pump without the need for pipes and elbows. Lobe pumps should preferably have an enlarged top rectangular port for easier soap entrance into the pump.

The vapors generated from VLS systems, in spite of their low pressure, can be reused for heat recovery purposes, depending on the plant configuration and the types of soaps produced:

- In this application, the vapors from the VLS can directly drive a properly configured steam booster (Figure 7.9), thanks to the favorable mass rate between vapors from the VLS and balance vapors from the vacuum chamber. It is possible to achieve a consistent 10–15 torr vacuum improvement compared to the same plant working without the booster, without consumption of fresh makeup steam. Fresh steam is used normally only for start-up and/or transitory conditions.
- The liquid neat soap can be preheated up to 110–120 °C in a dedicated heat exchanger placed before the heat exchanger of the vacuum dryer. Since not all the vapors from the VLS are used, the remaining can be used to heat up the makeup water for the boiler, the raw materials, and the soap storage tanks.
- It is possible to use the VLS vapors to preheat the raw materials used in a continuous saponification plant, if one is installed nearby. Refer to alternate B in Figure 7.9.

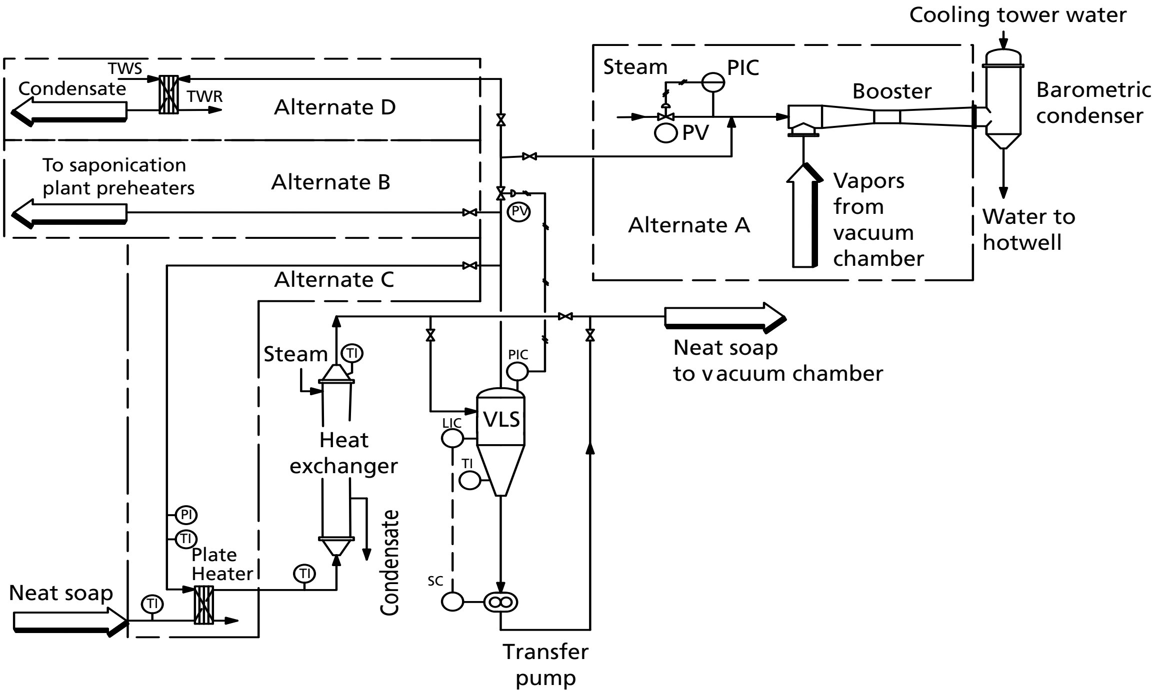


Figure 7.9 Mazzoni LB alternate VLS heat recovery option.

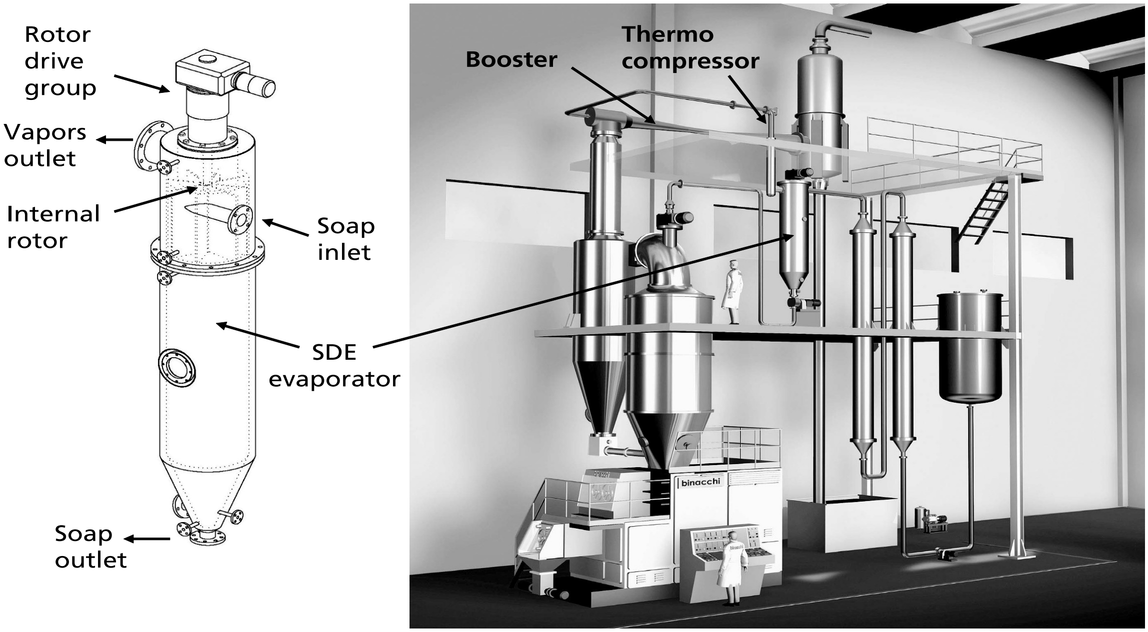


Figure 7.10 Binacchi soap dryer evaporator (SDE) application.
Source: Binacchi & Co.

Binacchi Soap Dryer Evaporator (SDE) System

Binacchi's soap dryer evaporator (SDE) system consists of an evaporator with rotating inner parts and an intermediate thermocompressor unit (Figure 7.10). The vapors are recompressed to an intermediate pressure in a thermocompressor using fresh steam, and the combined steam is then sent to the main booster. This setup allows vacuum levels lower than 30–35 torr to be obtained with limited steam consumption, which may be particularly helpful in the production of soap/synthetic combo products.

Additives Feeding Systems

Liquid additives and slurries can be injected into the neat soap going to the vacuum drying, generally just before the vacuum spray chamber itself. These additives (glycerine, superfatting agents, sodium silicate, talc/water talc/silicate slurry, etc) are dosed into the drying system using:

- Piston pumps for additives in small quantity
- Positive displacement (PD) pumps with mass flow meters and inverters for glycerine, superfatting agent, and sodium silicate solution
- Peristaltic pumps with inverters for talc/water or talc/silicate slurries

The flow rates of the pumps are coordinated, according to the production recipe, to the neat soap feed pump (stand-alone dryers) or to the raw material dosing pumps (integrated plants).

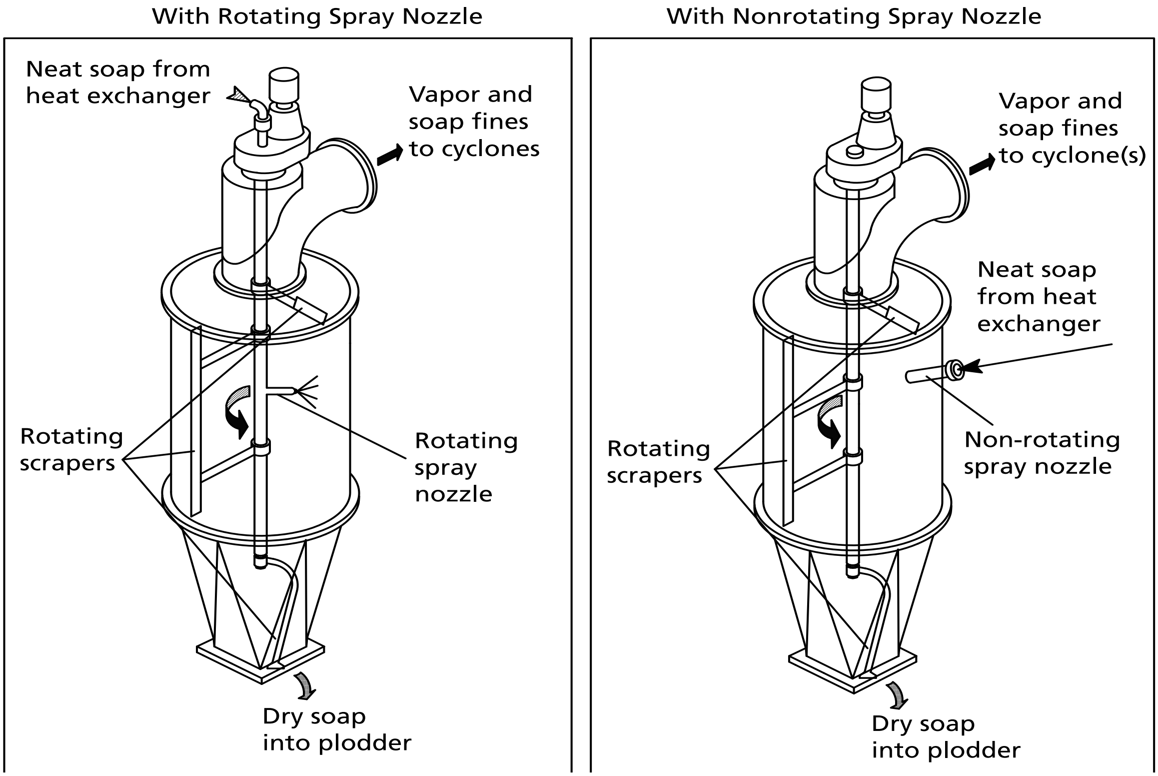


Figure 7.11 Vacuum chambers.

Vacuum Chambers

Two types of vacuum spray chambers are used for soap drying plants (Figure 7.11). The most widely used rotating-nozzle type is offered by all of the manufacturers of vacuum spray drying plants, with some variation in the design (number and position of nozzles, design of scrapers, shape of vapor outlet pipes).

Mazzoni LB's current standard is the innovative "no-spray" vacuum chamber, which features a tangential injection of the liquid soap in lieu of the spraying-nozzle technique of conventional units.

The no-spray technology offers the following production advantages: significant reduction of fines formation thanks to the absence of a spraying nozzle and reduåced carryover of fines due to an internal anti-entrainment baffle.

These two points result in a reduced contamination of the water flow from the barometric condenser. The new design of the no-spray vacuum chamber also demonstrates the following mechanical improvements compared to the conventional design:

- Significant reduction of the vacuum chamber's dimensions and simplification of the rotating components
- A simplified main drive shaft that doesn't require the internal soap pipe or mechanical seal on the main shaft

Soap Fines Recovery Systems

Various cyclone-type separators are used to recover the soap fines produced in the vacuum spray chamber.

Dual Cyclone

Two cyclones connected in series is the traditional system, commonly used today even for large dryers with capacities of 8–10 tons/h (Figure 7.12). In the past this technique was limited to smaller plants. Today the additional capacity is possible thanks to the reduction of dust carryover due to use of vapor separators and no-spray chambers. The soap fines recovered in the second cyclone are fed with a worm conveyor to the first cyclone, from which another worm conveyor feeds it to the vacuum spray chamber. Both worm conveyors are fitted with bridge breakers. To avoid recycling the fines into the vacuum chamber, a fines extruder can be installed under the first cyclone, and it is even possible to use a reversible single extruder/conveyor unit. The multicyclone design previously used as the second-stage cyclone has been abandoned in recent years, due to high investment and installation costs and more difficult cleaning.

Single Cyclone

A single large-size cyclone can be used for all laundry soap plants and for toilet soaps plants with capacities up to to 6,000 kg/h for tallow and coconut type soaps. For vegetable-based soaps, which generate more soap fines, this is less convenient.

Soap fines are not recycled to the spray chamber, but are discharged and collected in a drum, as is regularly done for laundry soaps but less often for toilet soaps. In this case, a second single cyclone still continuously feeds the fines to the first cyclone, from which the fines are discharged with a worm extruder conveyor. Because handling and reusing the

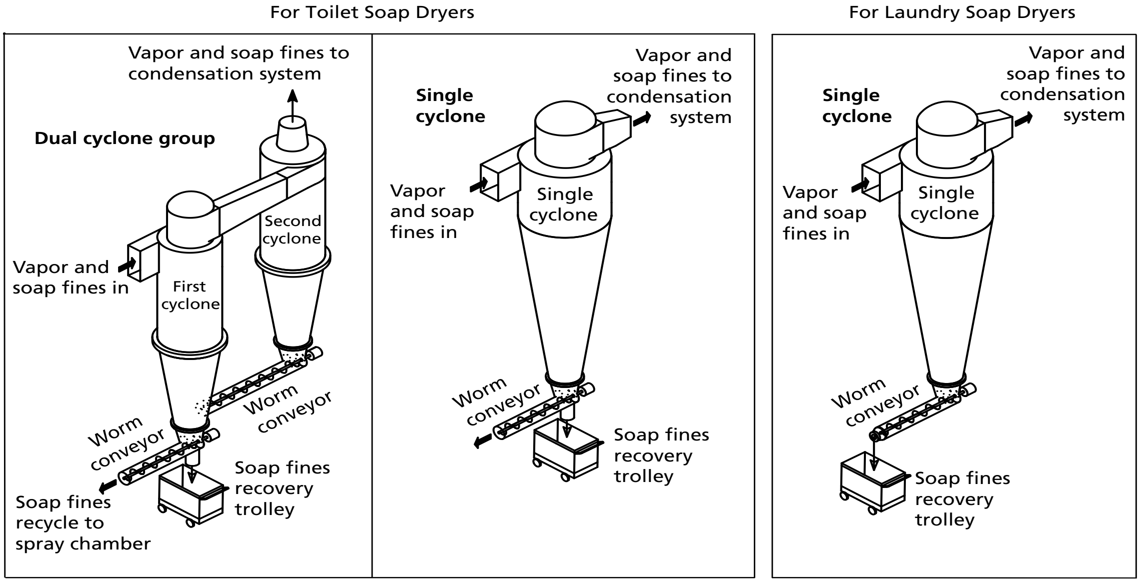


Figure 7.12 Soap fines recovery systems.

fines poses major problems, the noncontinuous recycle system for drying toilet soaps is seldom used.

Vacuum Producing Systems

Vacuum-producing systems for soap dryers consist of vapor condensation equipment (barometric and surface condensers and cooling tower systems) and vacuum-producing equipment (vacuum pumps and steam jet ejectors).

Vapor Condensation Equipment

The sole purpose of a condenser is to continuously condense the vapors generated during the drying process back into water. Three basic types of condensers are used: barometric, surface, and indirect condensers (see Figure 7.13).

Barometric Condensers

Barometric condensers are also called direct-contact condensers because they condense the vapors by direct contact with the cooling water. The condensed vapors, the cooling water used for condensation, and the soap fines are discharged together into a hot well. Contact condensers may be designed with water-spraying nozzles or with a traditional "plate" design. Carbon steel is a common construction material. When the cooling water

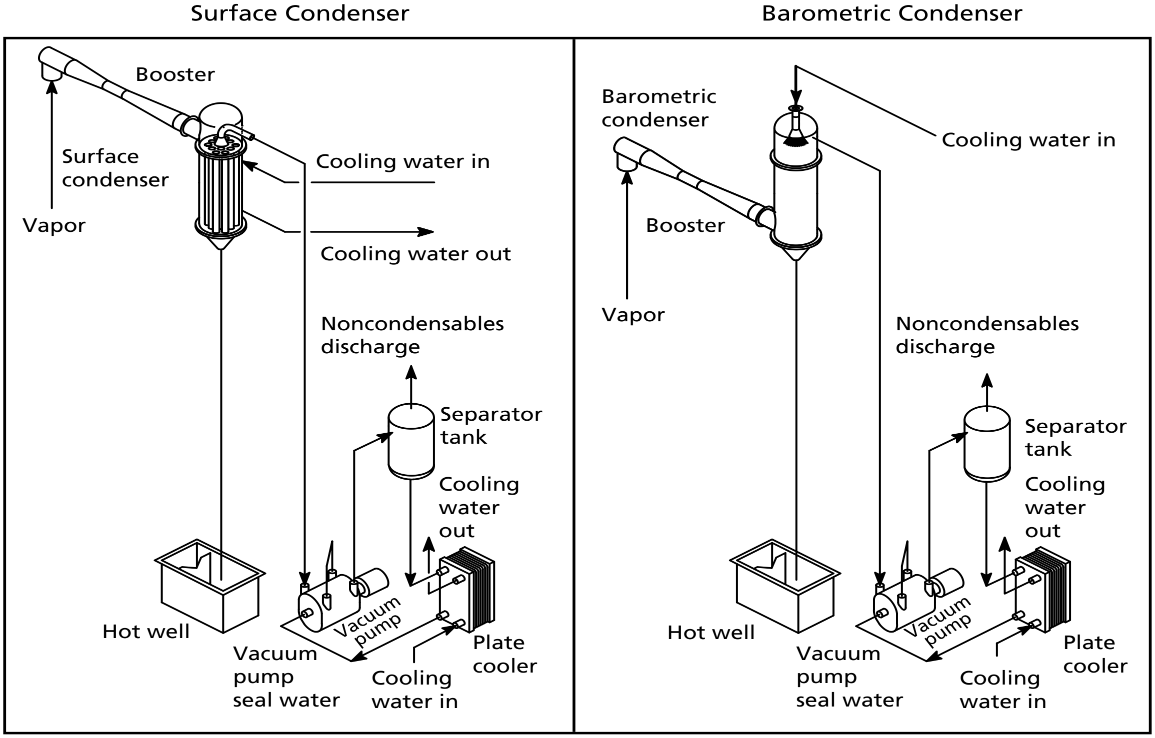


Figure 7.13 Vapor condensation and vacuum formation.

temperature is higher than 27 °C and pellet (noodle) temperature lower than 38 °C is required, then a steam booster must be used.

Surface Condensers

Surface condensers are shell-and-tube heat exchangers. The vapors flowing inside the tubes will be condensed by cooling water flowing on the shell side. The cooling water is not contaminated with the soap fines because it does not contact the process side. The condensed vapors that carry the final traces of soap fines are discharged into the hot well, and the clean water, free from soap fines, is recycled. To limit the size and cost of a surface condenser, the cooling water temperature should not exceed 20 °C. The cooling water can be efficiently used in a closed circuit, using a cooling tower in conjunction with a water

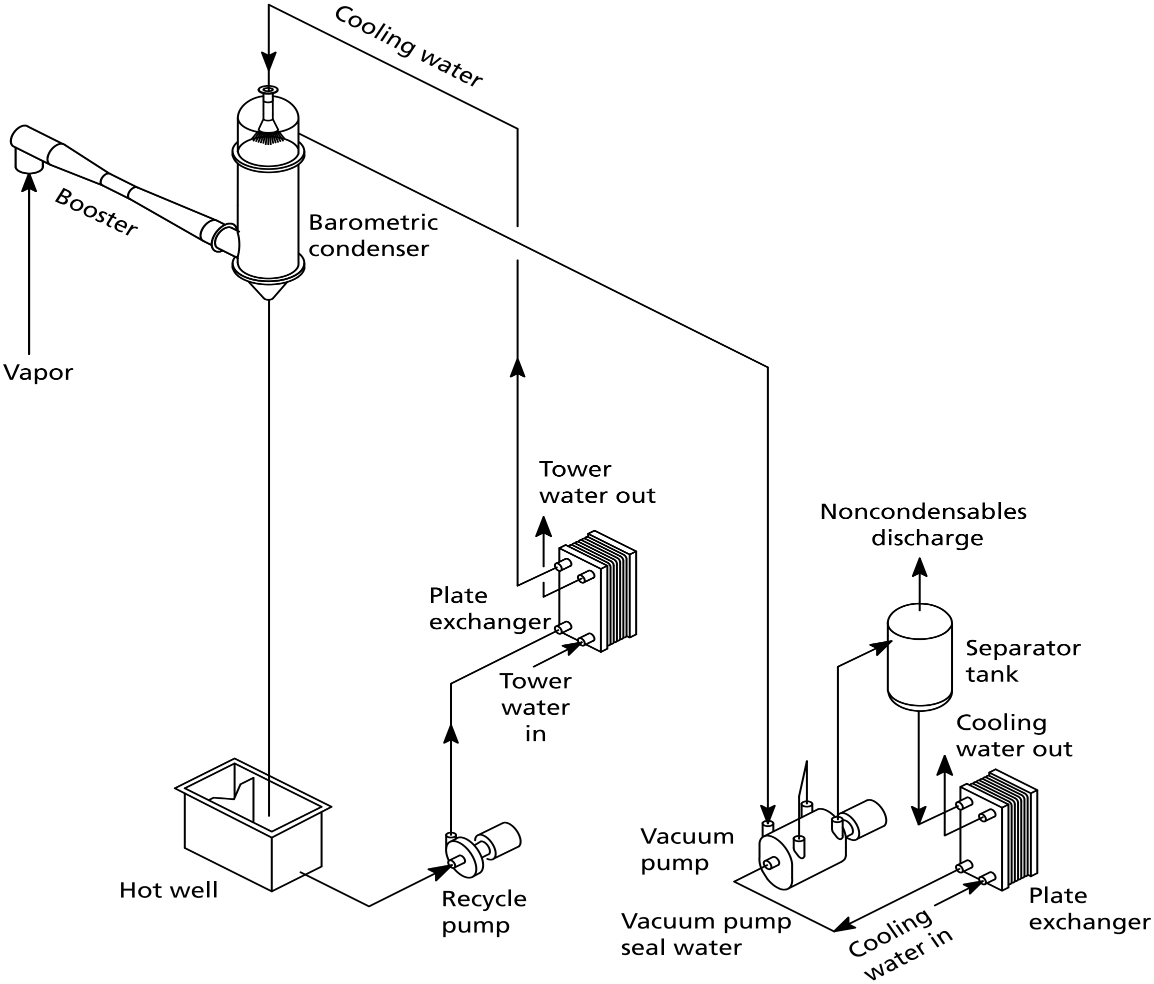


Figure 7.14 Indirect condensation system (ICS).

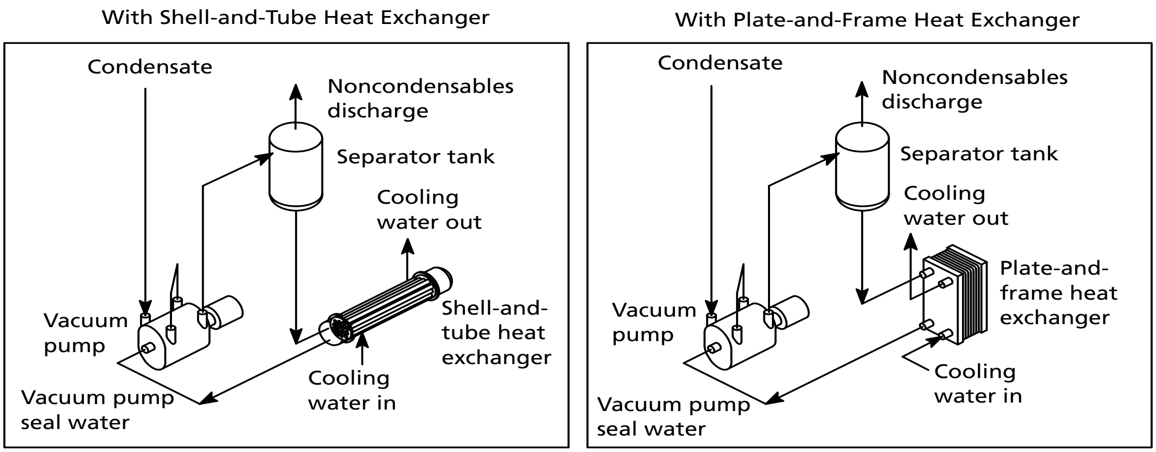


Figure 7.15 Vacuum formation systems.

chiller. Surface condensers can also be mounted at a lower height than barometric condensers, using a collecting vessel under vacuum and a self-priming pump.

Indirect Cooling Water System

The indirect cooling water system (ICS) (Figure 7.14) is an alternative system to the previously described surface and barometric types (Figure 7.15). The ICS system consists of a centrifugal pump to circulate water in a closed loop between the hot well and a barometric condenser, passing through a plate heat exchanger that cools down the recycled water with the cooling tower water. Due to the high heat transfer rate obtained with the plate heat exchanger, this is an economical system which can also be operated with cooling water that exceeds 30 °C temperature.

This system avoids contamination of the cooling tower like one that uses a surface condenser, but it offers two major advantages:

1. Lower investment and installation cost
2. Less frequent cleaning, once a month instead of every week or two weeks for the surface condenser type.

Vacuum Formation Systems

Vacuum Pumps

Mechanical piston pumps, used extensively years ago, are practically abandoned today due to their high cost, and liquid ring pumps are now the preferred choice. They are available on the market as a skid-mounted complete group, with gas/liquid separators and plate coolers or shell-and-tube heat exchangers to maintain the seal water at the lowest possible temperature based on local conditions (Figure 7.15). In some plants, steam ejectors are used to replace the liquid ring vacuum pumps. Steam ejectors are cheaper and require virtually no maintenance, but operational costs (motive steam) are higher.

Steam Jet Ejectors (Boosters)

Steam jet ejectors are very simple devices consisting of a nozzle, a mixing chamber, and a diffuser. Single-stage ejectors are generally used for soap drying plants. Steam boosters are generally employed for laundry soap making, where the necessary vacuum cannot be achieved only with cooling water and vacuum pump. For toilet soaps, generally it is accepted to produce pellets at a slightly higher temperature in order to save the huge costs of steam for the booster.

Special Vacuum Groups

Special vacuum groups available on the market, composed by a root blower and a liquid ring vacuum pump, allow a double suction flow rate compared to a liquid ring vacuum pump having the same installed power. This further improves the vacuum achievable and therefore:

- For toilet soap, pellets colder by 2–3 °C, compared to a plant with a liquid ring vacuum pump, can be produced
- For laundry soap, due to the lower residual pressure (vacuum) achievable in the barometric condenser, the steam booster motive steam consumption can be cut down by 50%.

Plant Automation

Instrumentation and Computer Control

Electronic instrumentation is now standard for soap drying installations. The majority of new plants are computerized, and existing ones are converted to computer control. Besides computer control, a modern drying plant should include the following main features:

- Feed tank level control, a level transmitter operating on the inverter of the soap transfer pump from storage, in order to keep the level in the feed tank stable
- Soap flow control loop using a magnetic or mass flow meter
- Steam pressure control loop (independent for any single heat exchanger)
- Vacuum chamber residual pressure transmitter (mm Hg or mbar)
- Soap spraying pressure control (for no-spray chambers)
- Soap level in VLS
- Pressure in VLS
- Vacuum in the spraying chamber
- Temperature at inlet/outlet of cooling water to condenser

In integrated plants, the control system is combined with the saponification section.

Computer control systems (CCS) are used for soap dryer process control. CCS based on hardware consisting of PC and PLC are favored because of lower investment costs and similar capability compared to more costly distributed control systems (DCS), which are more suitable for larger plants (such as those in the petrochemical industry, for example). For small plants, the PC can be replaced by an operator panel integrated into the electrical panel board.

Depending upon the provided field instrumentation, the CCS memorizes production recipes and operating conditions; summarizes consumption of neat soap, additives, and so on; and records process parameter trends. It also performs emergency procedures and alarm detection.

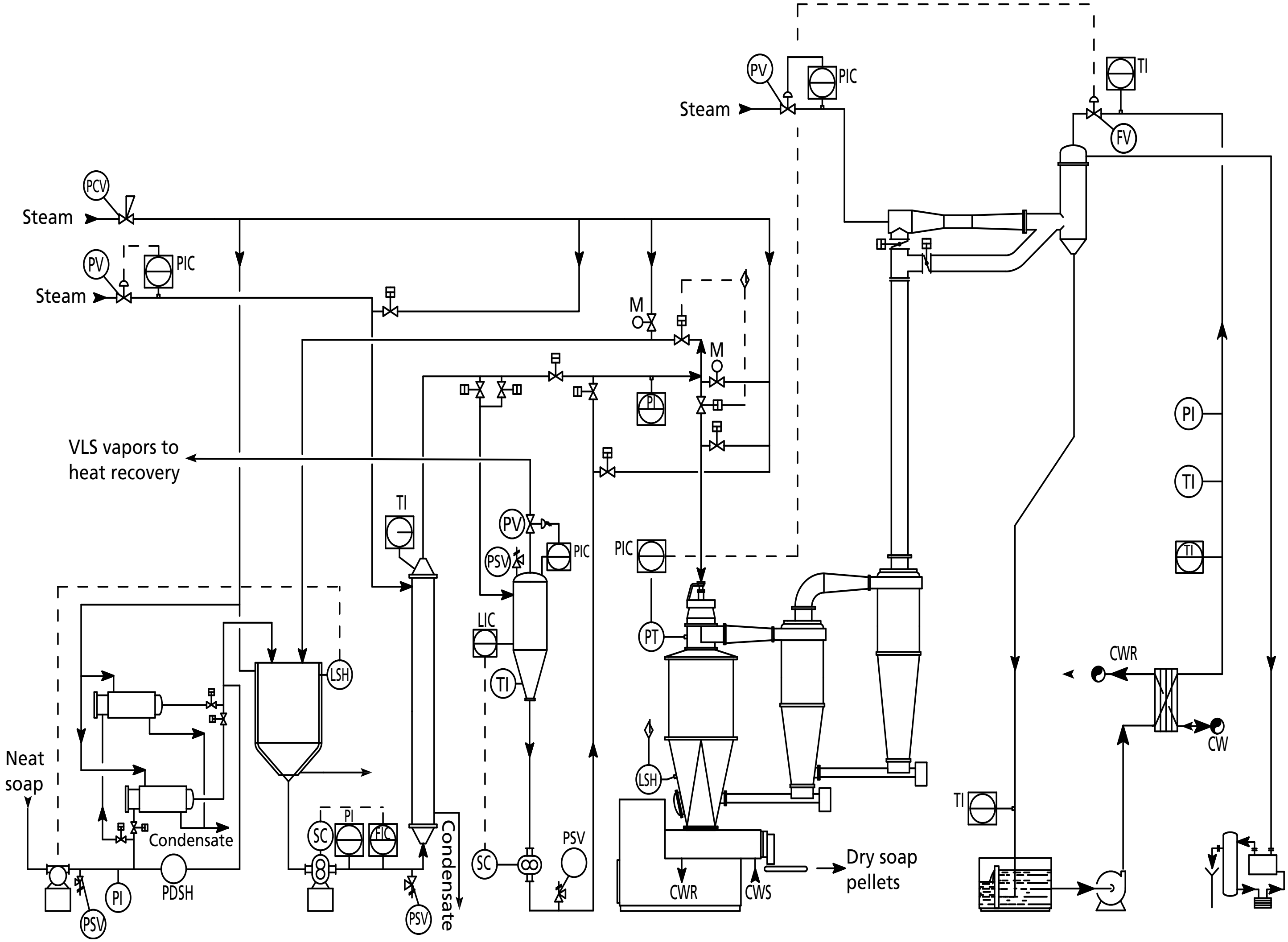


Figure 7.16 Soap drying plant automation and control.

Safety interlocks are used for all motors, doors, high soap levels in the vacuum chamber, and so on. A soap-recycle mode is used for efficient start-up and shutdown or in emergencies, using an automatic set of valves that allow the operator to pump the soap from the heat exchanger back to the feed tank. Once the proper temperature is reached, the soap is fed to the spray chamber. Steam cleaning of all the soap pipes with automatic or computerized steam injection valves is part of the overall system. Figure 7.16 (p. 155) shows the flow diagram of a complete, fully instrumented, automated dryer with VLS booster with bypass.

Neat Soap Flow Control

The use of mass flow meters or magnetic flow meters is becoming very popular, since it offers the following important advantages (Figure 7.17):

- Instantaneous control of neat soap feed flow rate and monitoring (per shift, day, week, etc.)
- Synchronization of neat soap flow rate with other additives, flow rates
- Easy detection of anomalous conditions (such as "no-flow") with consequent activation of proper alarms/interlocks

On Line NIR Analyzer

A NIR (near infrared) analyzer, positioned near the outlet of soap pellets/bars from the plodder, can be used for continuous measurement of:

- Soap moisture
- Soap free alkalinity/acidity

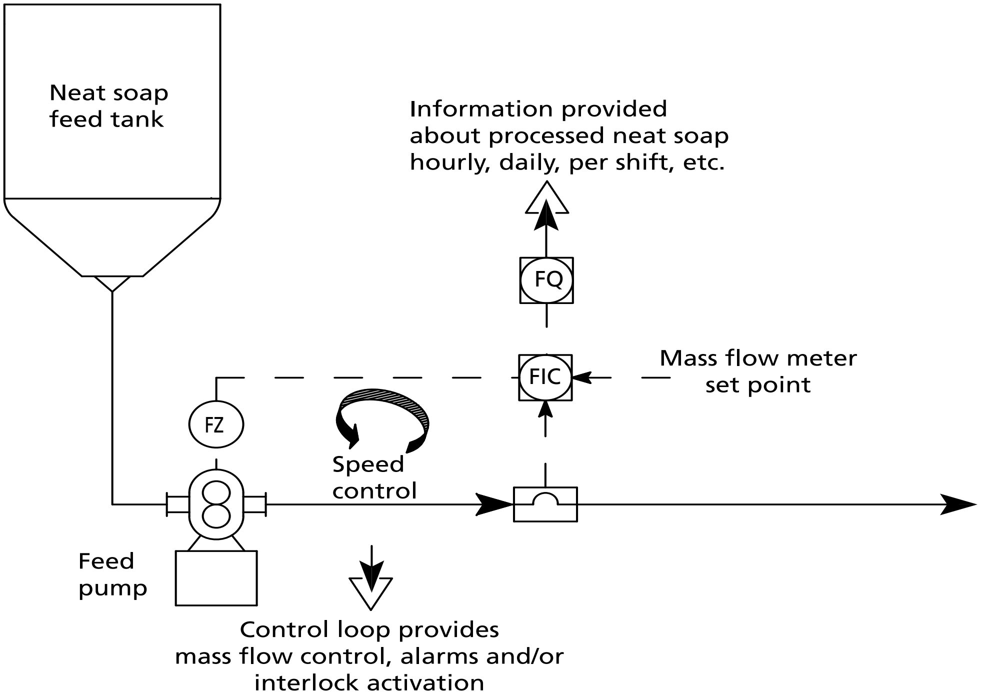


Figure 7.17 Neat soap flow control with mass flow meter.

Mazzoni LB has applied this system, developing calibration curves for the most common types of toilet and laundry soaps. The NIR measurements can be used for process automation as follows:

	Stand-Alone Dryers	**Integrated Dryers**
Moisture	Action on the automatic steam control valve to the heat exchanger	Action on the automatic steam control valve to the heat exchanger (where foreseen) or on the water flow rate to the reactor (integrated plant)
Free alkalinity/ Acidity	—	Action on caustic soda flow rate to the reactor.

Due to the high measurement accuracy, this technique allows for major reduction of the manual analytical control during production.

Intensive sampling is necessary at the installation of the analyzer to correlate the readings of the instrument with the standard laboratory analysis. Due to the high required investment cost, this system is recommended only for large-capacity plants.

Appendix

This appendix includes the following:

- Definitions and terminology relating to drying and heat transfer
- Material balance calculations (Equation 7.1, p. 161) and graphs for liquid neat soap to dry toilet soap pellets (Figure 7.18, p. 158) and laundry soap bar conversions (Figure 7.19, p. 159)
- Formulas for calculating the amount of water evaporated (flashed off) under vacuum and pre-evaporated in the heat exchanger (Equations 7.2 and 7.3, p. 161), and a graphic illustrating toilet soap dried to different moisture levels (Figure 7.20, p. 160)
- The well-known formulas for heat exchanger duty (Equations 7.4 and 7.5, p. 161) and/or heat transfer coefficient calculation for sizing a heat exchanger (Equation 7.6, p. 161)
- Overall material balances for toilet soap (with and without VLS) and laundry soap drying (Figure 7.21, p. 160; Figures 7.22 and 7.23, p. 162).
- A guide to determine the actual operation vacuum (absolute pressure) and the relationship to the condensed water discharge temperature (downleg temperature) into the hot well in a drying system with a barometric or a surface/indirect condenser
- Total fatty matter (TFM) and moisture content (%) calculation table for toilet soaps (Table 7.3, p. 165)

Definitions and Terminology

Density: The density or specific weight of a fluid is its weight per unit of volume. The density of common neat soap base is 59.3–62.4 lb/ft^3 (950–1000 kg/m^3).

Specific gravity: The specific gravity of a fluid is the ratio of its density to the density of water (dimensionless).

Vapor pressure: The vapor pressure of a pure liquid is the pressure (at a given temperature) at which a liquid will change to a vapor. If this liquid is mixed with nonboiling substances (e.g., water with soap), the vapor pressure must be corrected by the mole fraction of water.

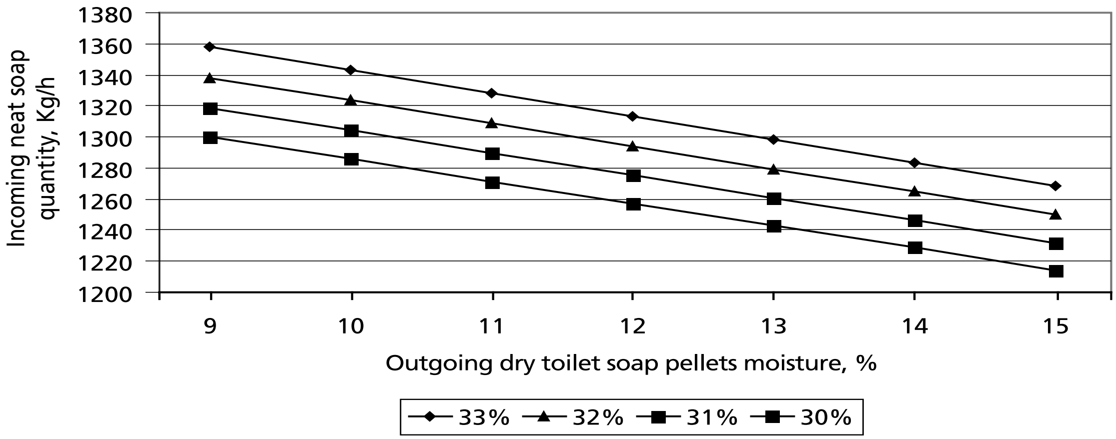


Figure 7.18 Toilet soap mass balance per 1000 Kg/h of dried product.

***Viscosity**:* The viscosity of a liquid is a measure of its tendency to resist a shearing force. Neat soap behaves as a non-Newtonian fluid exhibiting a nonlinear shear stress/shear rate behavior. Its viscosity decreases with increasing shear rate (velocity).

Velocity		Viscosity
(Feet/sec)	(Meters/sec)	(Centipoise)
0	0	2000–3000
0.5	0.15	1000
1.0–2.0	0.3–0.6	300–500

Viscosity of 30–32% moisture content 90 °C temperature neat soap at different pumping speeds.

Specific heat (Cp): The specific heat of a substance is the amount of heat necessary to raise the temperature of a unit mass by one degree. The following formula is used to calculate the amount of heat gained (lost) by a given mass due to a change in temperature:

$$Q = m \times Cp \times \Delta T$$

where Q is the amount of heat (kcal), m is mass (kg), Cp is the specific heat (kcal/kg/°C), and ΔT is the change in temperature (°C). The specific heat is calculated according to the water content in the neat soap using the following formula:

$$Cp = 0.6 \times \% \text{ anhydrous soap} + 1 \times \% \text{ H}_2\text{O}$$

Specific Heat (Btu/lb/°F) or (Kcal/kg/°C)	%TFM
0.73	63
0.68	73
0.64	84

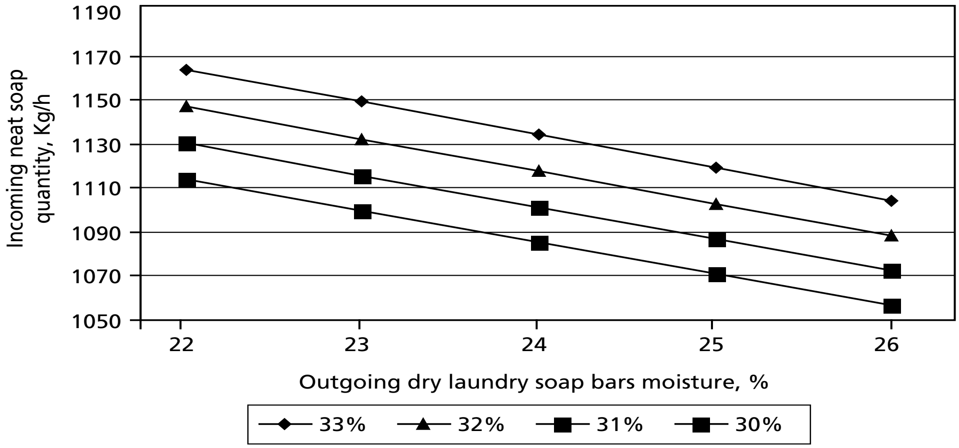


Figure 7.19 Laundry Soap Mass Balance per 1000 Kg/ of Dried Product

Thermal conductivity (k): This value depends on the water content and is expressed by the formula

$$k = (0.58 \times W) \times 0.9 + (0.15 \times S) \times 0.9$$

where S = % of soap and W = % of water. k is expressed in kcal/m/°C.

Sensible heat: The sensible heat (kcal/kg) is the heat necessary to increase the temperature of a liquid from an initial to a final temperature without starting evaporation of the liquid. For example, it takes 100 kcal to bring the temperature of 1 kg of water from 0 °C to 100 °C, and this is calculated as follows:

$$SH = 1\text{ kg} \times 1\text{ kcal/kg/°C} \times (T_{\text{final}} - T_{\text{initial}}) = 1 \times 1 \times (100 - 0) = 100\text{ kcal/kg}$$

Here 1 kcal/kg/°C is the specific heat of water.

Latent heat of vaporization: The latent heat of vaporization (kcal/kg) is the heat that produces a change of state (e.g., from liquid to vapor) without a change in temperature. For example, it requires 540 kcal to convert 1 kg of water at 100 °C to 1 kg of steam at 100 °C.

Material Balances

In the soap industry, the production of soap dryers refers to the plant output at a given moisture. The quantity of incoming liquid neat and the resulting quantity of finished product at various moisture levels is given by Equation 7.1 (p. 161), and it is represented for pure toilet and laundry soaps in Figures 7.20 and 7.21.

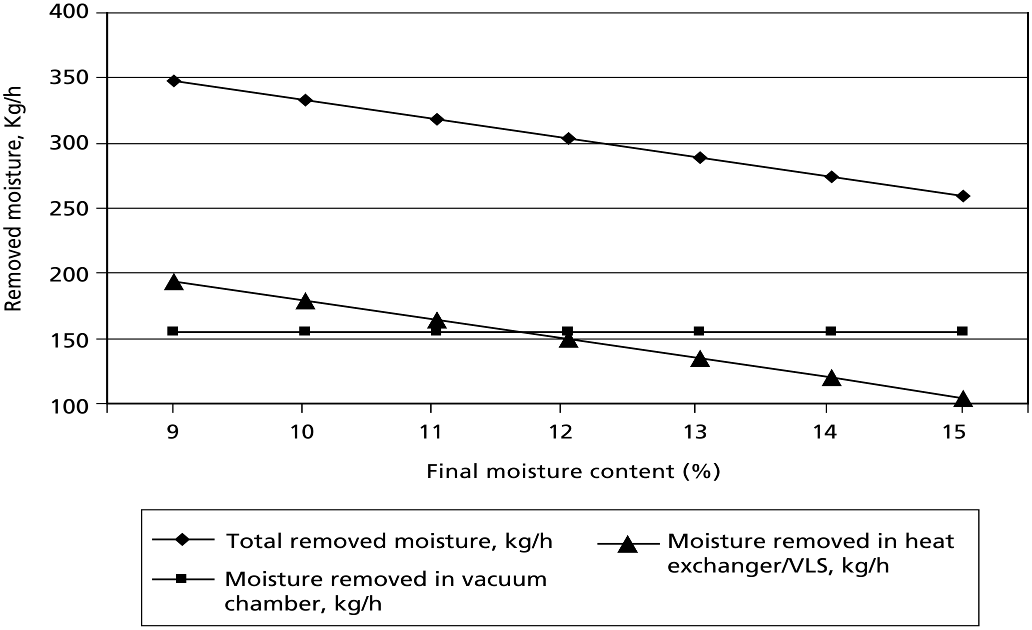


Figure 7.20 Moisture removal distribution from toilet soap starting from 32% neat soap.

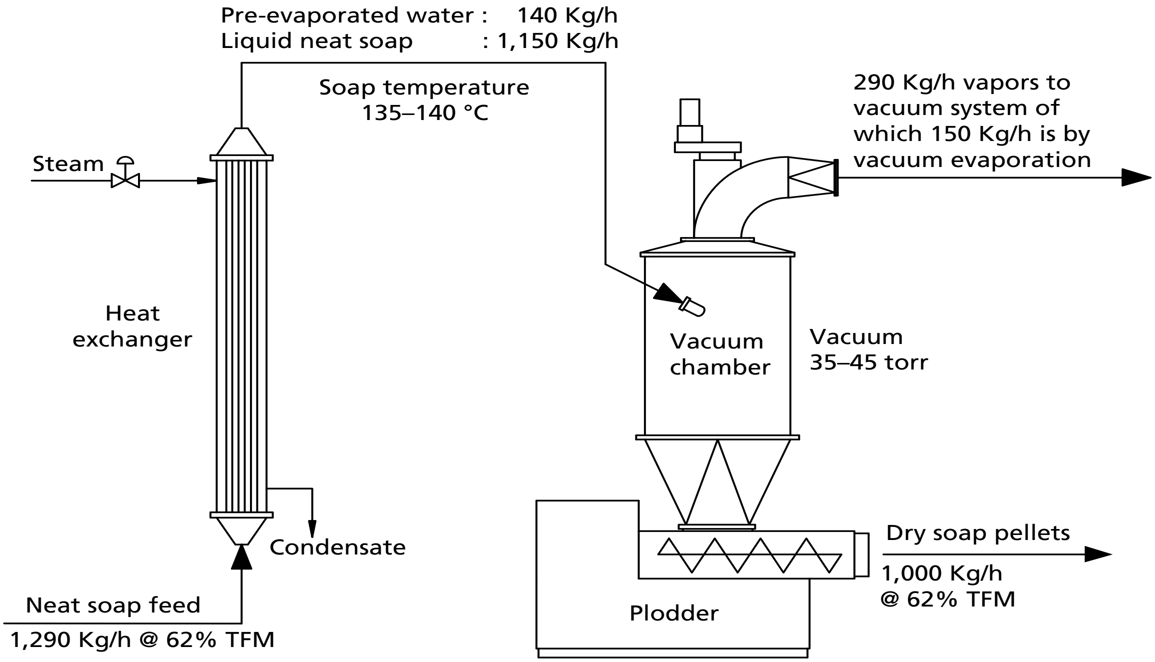


Figure 7.21 Toilet soap drying material balance.

$$G_{in} = G_{out}\,(100 - M_{out})/(100 - M_{in}) \qquad \text{(Eq. 7.1)}$$

where

G_{in} = incoming neat soap quantity (kg/h)
G_{out} = outgoing dry soap quantity (kg/h)
M_{in} = incoming neat soap moisture (%)
M_{out} = outgoing dry soap moisture (%)

The quantity of water evaporated by vacuum expansion is

$$W_v = G_{in} \times Cp_{he} \times (T_{he} - T_{vc})/LH_v \qquad \text{(Eq. 7.2)}$$

where

W_v = quantity of water evaporated by vacuum expansion (kg/h)
LH_v = latent heat of water at vacuum chamber conditions (kcal/kg)
Cp_{he} = specific heat of soap at heat exchanger outlet (kcal/kg/°C)
T_{he} = temperature of soap at heat exchanger outlet (°C)
T_{vc} = temperature of soap in vacuum chamber (°C)

The total amount of water to evaporate is

$$G_{total} = G_{in} - G_{out}$$

The water to be pre-evaporated in the heat exchanger is

$$W_{he} = G_{total} - W_v \qquad \text{(Eq. 7.3)}$$

When the plant includes a VLS, it can be assumed that all this water is removed in the VLS before soap enters into the vacuum chamber. In most cases, the water eliminated in the VLS is slightly more, due to a small expansion between the outlet of the heat exchanger and the VLS.

The heat exchanger duty is the sum of the following two partial duties:

$$\text{Sensible heat} = G_{in} \times Cp\,(T_{he} - T_{in}) \qquad \text{(Eq. 7.4)}$$

$$\text{Latent heat} = W_{he} \times LH_{he} \qquad \text{(Eq. 7.5)}$$

where LH_{he} = latent heat of water in the heat exchanger (kcal/kg).

The amount of water evaporated (flashed) by expansion into the vacuum spray chamber and the quantity pre-evaporated in the heat exchanger, per Equations 7.2 and 7.3, is illustrated in Figure 7.21 for 32.5% moisture content neat soap and dry toilet soap pellets at different moisture levels.

The overall material balance for dry toilet soap pellets produced from neat soap with a single-stage vacuum spray dryer (with and without the VLS) is summarized in Figures 7.21 and 7.22. Balance for laundry soap bars is represented in Figure 7.23.

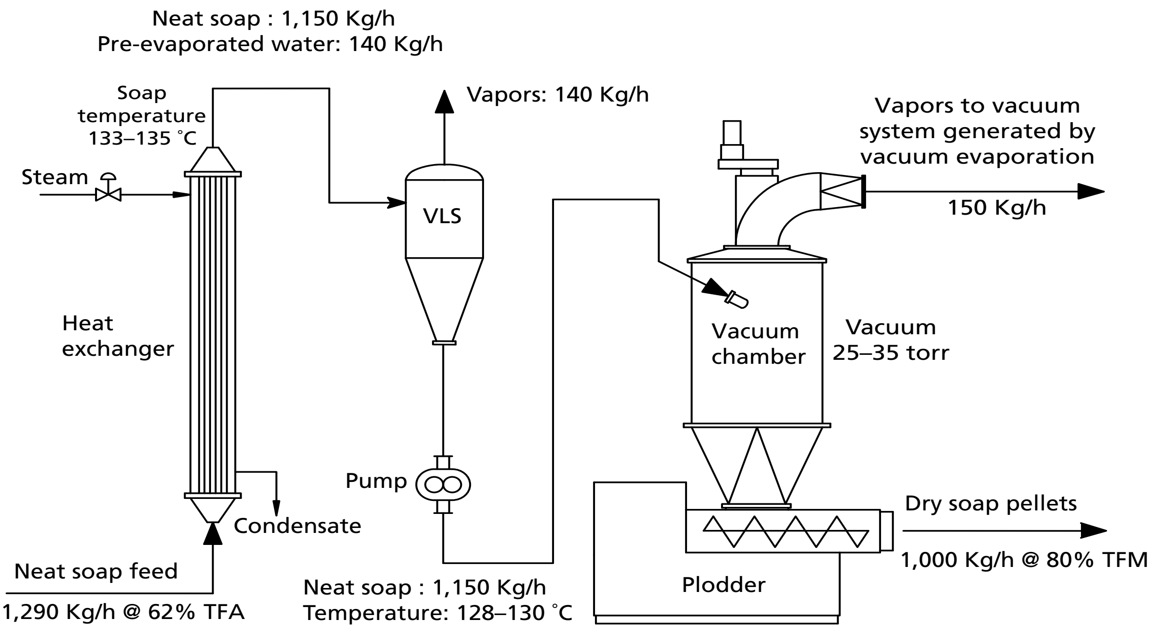


Figure 7.22 Material balance for toilet soap drying with VLS system.

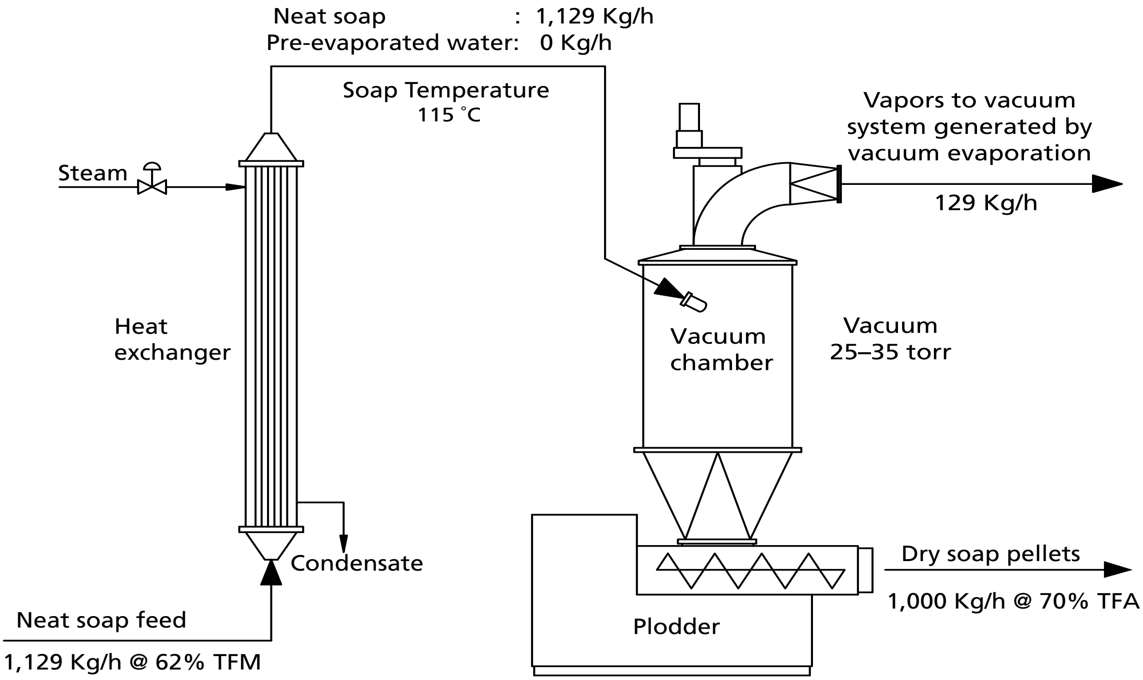


Figure 7.23 Laundry soap drying material balance.

Heat Transfer Rate

Soap behavior is pseudo-plastic, and its viscosity range under shear is from 50 to 100 cps at working temperatures in the heat exchanger. The global heat transfer rate, tube side, is calculated by the following quantities

Reynolds number: $Re = DVp/\mu$
Nusselt number: $Nu = hdlk$
Prandtl number: $Pr = Cp\mu/k$

using the following formula:

$$(hd/k) = 1.86\ [(Re)(Pr)(d/l)]1/3\ (\mu/\mu p\ )0.14$$

The value of h can be determined and substituted in

$$U = 1\ (1/h + x/ks + 1/hv)$$

obtaining the overall heat transfer rate, where

D = tube diameter (mm)
V = velocity of soap flow (m/s)
p = density (kg/m^3)
$\mu/\mu p$ = viscosity in *cPoise* × 3.6
d = equivalent diameter (mm)
k = thermal conductivity (Kcal/m × h × °C)
Cp = specific heat (Kcal/kg × °C)
L = tube length (cm)
h = heat transfer coefficient (soap side) (Kcal/m^2 × *h* × °C)
hv = heat transfer coefficient (steam side) (Kcal/m^2 × *h* × °C)
x = tube wall thickness (mm)
ks = steel thermal conductivity (Kcal/m × *h* × °C)
U = overall heat transfer coefficient (Kcal/m^2 × *h* × °C)

Except for the production of a few types of laundry soaps, the water evaporated by expansion under vacuum is normally not enough for industrial drying purposes. The rest of the water must be pre-evaporated in the heat exchanger. Heat transfer areas utilized for vacuum dryer shell-and-tube heat exchangers are 20, 25, or 30 m^2/ton of dry soap; the size selected depends on the dry soap's final moisture and the product type.

Laminar flow is assumed for calculating the required heat transfer area. This allows for an adequate safety margin, since turbulent flow occurs when water starts boiling (pre-evaporation) in the heat exchanger.

Applying the equation

$$U = 1\ /\ (1/h + x/ks + 1/hv)$$

we see that the heat transfer coefficient U is in the range of 80–200 Kcal/m^2 × h × °C. The average value utilized is 150 Kcal/m^2 × h × °C.

Practical experience indicates that a minimum 4–5 cm/s velocity must be considered for soap inlet into the heat exchanger tubes. This speed will avoid preferential flow of the soap to the central tubes and allow some chocking the other tubes.

Operating Vacuum (Absolute Pressure) and Condensate Temperature

With Barometric Condenser

For plants with direct-contact barometric condensers, it can be estimated that the residual pressure in the vacuum spray chamber will be that corresponding to the vapor pressure of condensate (cooling water + condensate process vapors) at the downleg temperature, increased by 3 °C.

Example:

- Cooling water temperature into barometric condenser: 30 °C
- Condensate temperature into hotwell (downleg temperature): 34 °C
- Vapor pressure of water at 34 °C (absolute pressure): about 41 torr (Table 7.2)
- Actual vacuum in the dryer at 34 °C + 3 °C = 37 °C: about 47 torr (Table 7.2)

With Surface Condenser and ICS

For noncontact surface condensers, it can be estimated that the residual pressure in the vacuum spray chamber will be that corresponding to the vapor pressure of condensate process vapors at the downleg temperature, increased by 2 °C. A pressure drop of 2–3 torr through the unit also must be taken into account.

Example

- Cooling water temperature into surface condenser or water temperature from ICS plate cooler: 30 °C
- Cooling water temperature from surface condenser (or water temperature to ICS plate cooler): 34 °C
- Condensate temperature into hotwell (downleg temperature): 37 °C
- Vapor pressure of water at 37 °C (absolute pressure): 47 torr (Table 7.2.)
- Actual vacuum in the dryer at 37 °C + 2 °C : 39°C: about 54 torr (Table 7.2.)
- Plus 3 torr due to pressure drop, or 54 torr + 3 torr: 57 torr

Table 7.2 Vapor Pressure of Water

Temperature °C	Absolute Pressure torr	Temperature °C	Absolute Pressure torr	Temperature °C	Absolute Pressure torr
0	4.6	27	26.7	36	44.6
5	6.5	28	28.3	37	47.1
10	9.2	29	30	38	49.7
15	12.8	30	31.8	39	52.1
18	15.5	31	33.7	40	55.3
20	17.5	32	35.7	41	58.3
22	19.8	33	37.7	43	64.8
24	22.4	34	39.9	44	68.3
26	25.2	35	42.2	45	71.9

Total Fatty Matter (TFM) and Moisture Content of Toilet Soaps

Assumptions

- 80:20 tallow/coco mixture with an average 216 acid value
- Average molecular weight (MW): 56,100/216 = 260
- 63% TFM neat soap contains 0.40% glycerine, 0.05% NaOH, and 0.35% NaCI

Sample Calculation and Formulas

$$\begin{array}{lcl} \text{Fatty acid + Caustic soda} & \rightarrow & \text{Soap + Water} \\ RCOOH + NaOH & \rightarrow & RCOONa + H_2O \\ 260 + 40 & \rightarrow & 282 + 18 \end{array}$$

The ratio between TFM (or TFA) and anhydrous soap in this case is 282/260 = 1.0846. This means that neat soap with 63% TFM will in reality contain 63% × 1.0846 = 68.3% anhydrous soap (see Table 7.3).

Table 7.3 Total Fatty Matter and Moisture Content

TFM %	Anhydrous Soap %	Glycerine %	NaOH + NaCl %	Water %
58	63	0.4	0.4	36.3
59	64	0.4	0.4	35.2
60	65.1	0.4	0.4	34.1
61	66.2	0.4	0.4	33
62	67.3	0.4	0.4	31.9
63	68.4	0.4	0.4	30.8
64	69.5	0.4	0.4	29.7
65	70.6	0.4	0.4	28.6
66	71.6	0.4	0.4	27.5
67	72.7	0.4	0.4	26.4
68	73.8	0.4	0.4	25.3
69	74.9	0.4	0.4	24.2
70	76	0.4	0.4	23.1
72	78.2	0.5	0.5	20.9
74	80.3	0.5	0.5	18.7
76	82.5	0.5	0.5	16.5
78	84.7	0.5	0.5	14.3
80	86.8	0.5	0.5	12.1
82	89	0.5	0.5	9.9
84	91.2	0.5	0.5	7.7

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8 Bar Soap Finishing

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Introduction

The major advance for bar soap finishing has been the introduction of 500 to 600 bars per minute high-speed lines. To reach these speeds, "flashstamping" type presses with up to 16-piece die sets have been introduced.

Direct soap transfer devices, which are part of the presses, are directly coupled with one or two high-speed wrappers, cartoners, and flow wrappers. The use of PC/PLC controls for individual machines and for complete finishing lines has been widely accepted.

Processing Steps and Equipment

Processing Steps

Bar soap finishing consists of six processing steps for the production of standard, translucent, soap/synthetic (combo), and synthetic-type products.

1. Mixing the main dry soap base, mostly in pellet form, with minor liquid and solid ingredients
2. Refining the fully formulated mixture into a uniform, homogeneous product
3. Extruding the finished product into a compact slug (billet) of a predetermined shape and size
4. Cutting the extruded slugs into individual lengths as required by the soap press model used
5. Stamping the cut slug (billet) into a bar (tablet) of a specified weight and shape
6. Packaging the finished stamped bars

Mixing

There are no defined measuring criteria for mixing in the soap industry. *Macro* and *micro* are terms used in many industries, and we can apply these to soaps.

Macro Mixing

Mixing of 1–5% of solid and liquid ingredients with dry soap standard mixers (amalgamators) is macro mixing. During macro mixing, the additives mainly coat the outer surface of the pellets.

Micro Mixing

Double-arm sigma mixers and mixer-kneader-extruders are used for intensive micro mixing. Breaking up the soap pellets exposes more surface area and the liquid and solid additives penetrate the pellets more easily.

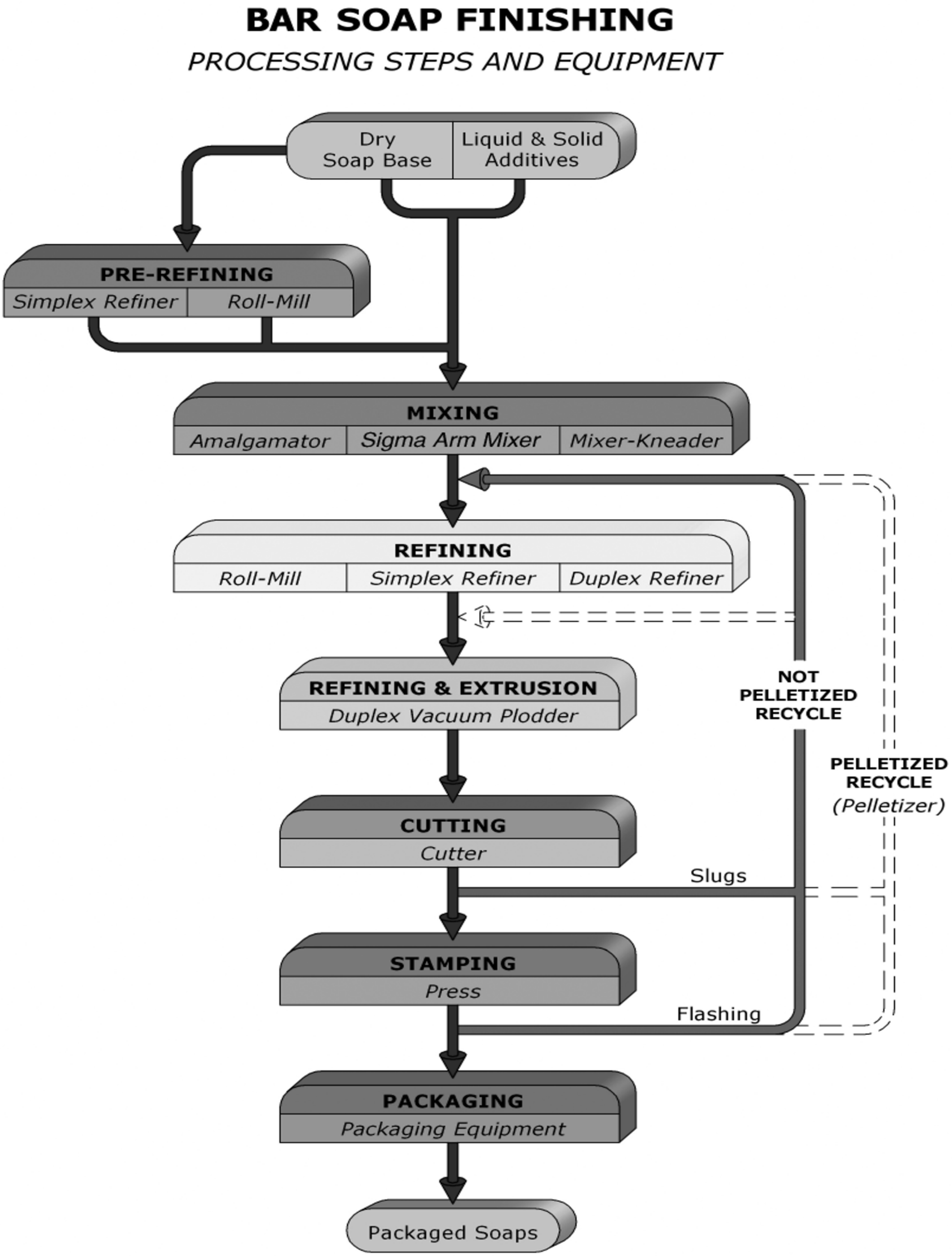


Figure 8.1 Bar soap finishing: Processing steps and equipment.

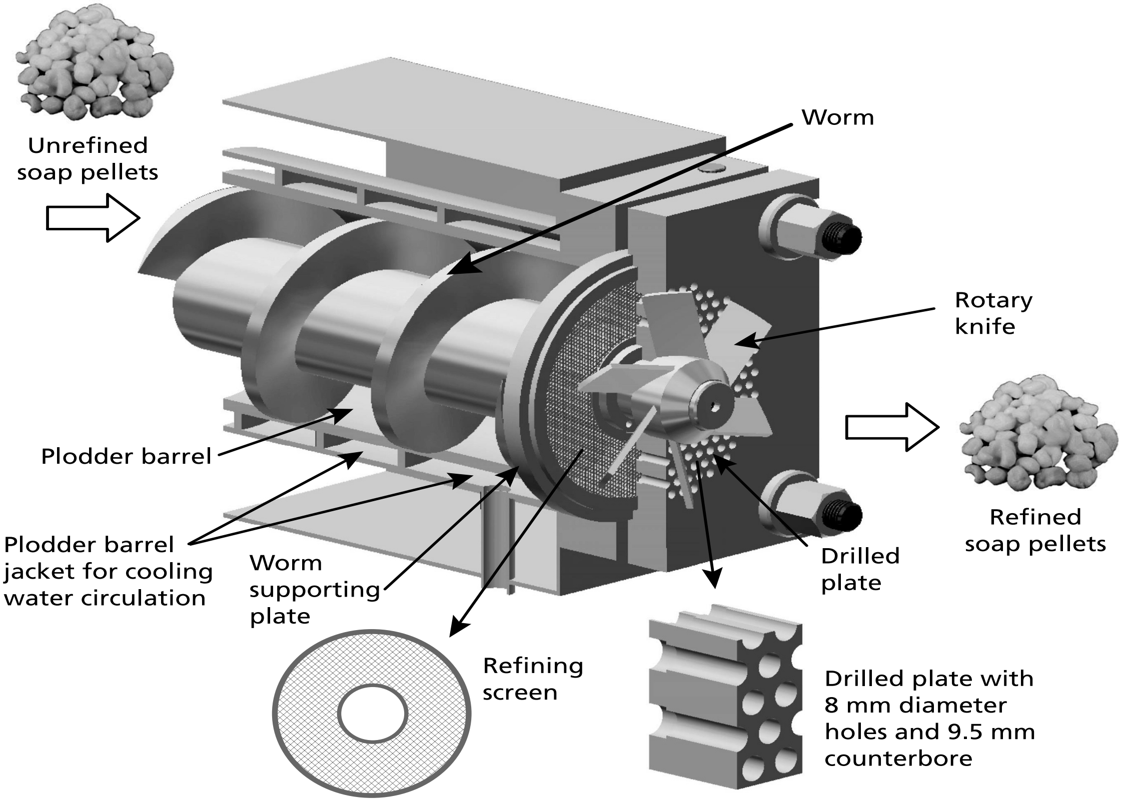


Figure 8.2 Plodder refining.

Refining

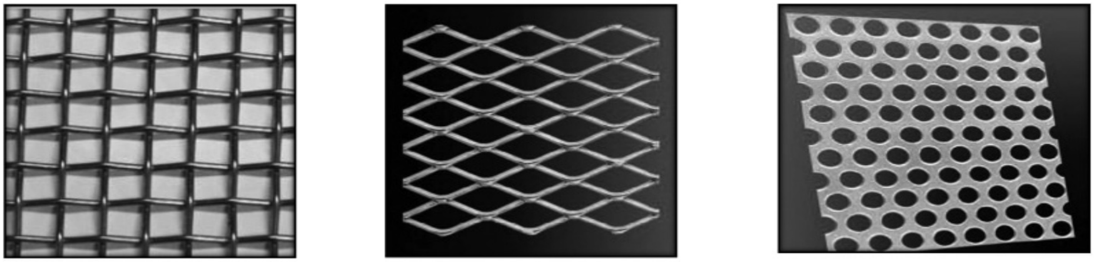
Refining is the work done on soap through the combined actions of pressure and shear. The purpose of refining is threefold:

1. To produce a fully homogeneous, uniform product
2. To improve bar feel by eliminating low solubility hard particles
3. To enhance product lather, solubility, and firmness by affecting crystalline structure change

Only plodders or plodders in combination with a roll mill are used for refining.

Plodder Refining

One full stage of refining is achieved when a plodder is fitted with a 50-mesh sized refining screen (Figure 8.2). When 20- or 30-mesh sized screens are used, the degree of refining is reduced. The most widely used refining screen is the square mesh wire type. Screen suppliers offer the same mesh-number screens with different wire diameters, widths of opening, and percentages of open area (Figures 8.3–8.6, and Table 8.1).

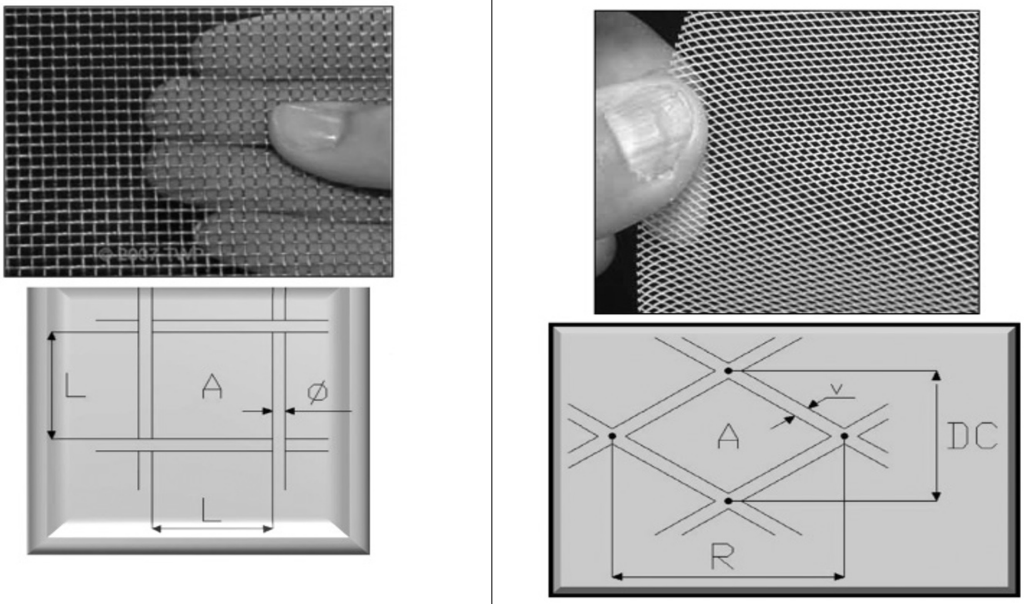


Wire mesh screen

Microexpanded metal

Perforated plate

Figure 8.3 Refining elements for plodders.



Wire mesh screen

Microexpanded metal

Mesh number: Number of openings per lineal inch (per 25.4 cm)

Width of opening (L): the size of clear opening between parallel lines

Wire diameter: ∅ (mm)

Open area: A (mm^2)

Strand thickness: V (mm)

Open area: A (mm^2)

Short diagonal distance: DC (mm)

Long diagonal distance: R (mm)

Figure 8.4 Wire mesh screen and microexpanded metal specifications.

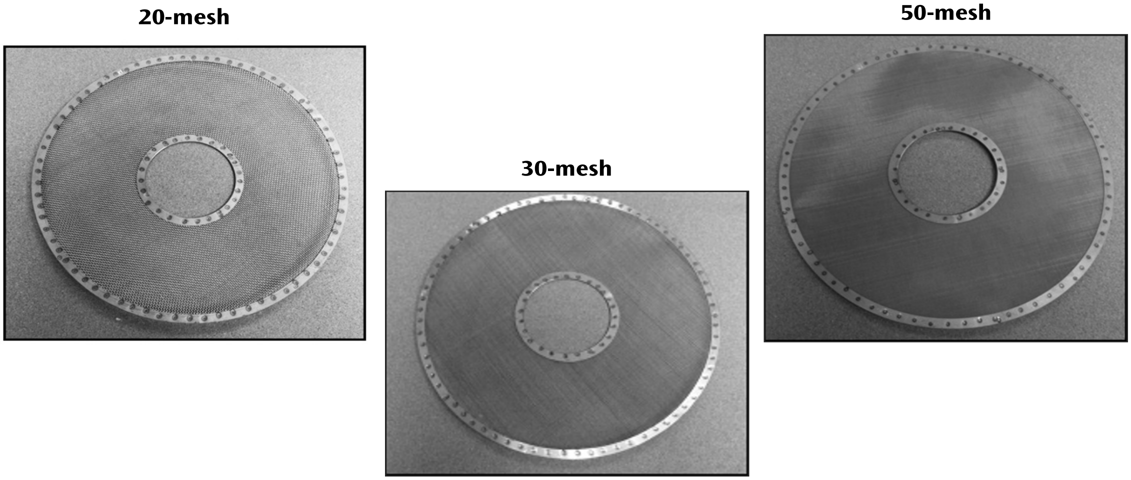
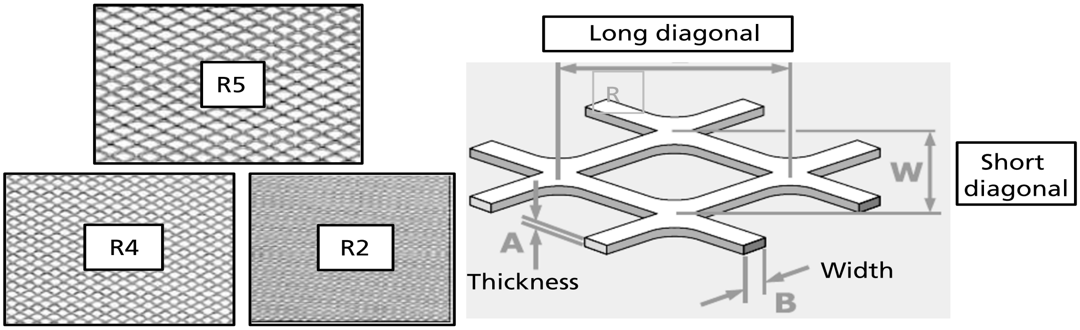
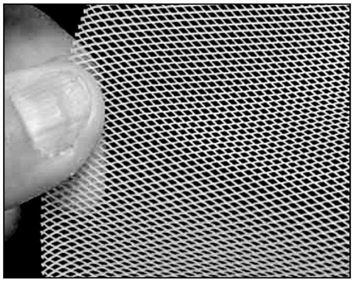


Figure 8.5 Examples of 20-, 30-, and 50-mesh screens.





Type	R Long diagonal	W Short diagonal	A Thickness	B Width	Open area %
R5	5	2.8	0.50	0.65	50–54
R4	4	2.2	0.50	0.50	44–48
R2	2	1.3	0.25	0.35	40–42

All dimensions shown are in mm.

Figure 8.6 Microexpanded metal screen specifications.

Table 8.1 Wire Mesh Screen Specifications

U.S. Mesh Number	Wire Diameter (inch/mm)	Width of Opening (inch/mm)	Open Area (%)
10	0.047 / 1.19	0.059 / 1.50	34.8
	0.032 / 0.81	0.068 / 1.73	46.2
	0.025 / 0.64	0.075 / 1.91	56.3
20	0.020 / 0.508	0.030 / 0.76	36.0
	0.018 / 0.320	0.032 / 0.81	41.0
	0.016 / 0.406	0.034 / 0.86	46.2
30	0.015 / 0.381	0.018 / 0.47	30.1
	0.013 / 0.330	0.020 / 0.52	37.1
	0.012 / 0.305	0.021 / 0.54	40.8
40	0.008 / 0.203	0.012 / 0.31	36.0
	0.009 / 0.229	0.011 / 0.28	30.3
	0.0075 / 0.191	0.0125 / 0.32	39.1

Table 8.2 Specifications for Perforated Plates with Round Holes

Round Hole Diameter (mm)	Holes per cm^2	Width (mm)	Open Area (%)
3.0	5	1.0	36
2.0	15	1.0	45
1.5	20	1.0	37
1.0	27	1.0	28
0.8	52	0.5	28
0.5	148	0.5	30

The degree of refining (homogenization and dispersion) of the minor ingredients into the main soap base by a roll mill depends on two variables: the roll gap (clearance or nip), which determines the soap flake thickness, and the shear generated by the roll speed differentials.

For most products, the gap between the last two rolls should be set at 0.15 to 0.20 mm for maximal performance. One must note that the actual flake (ribbon) thickness will be 0.05 to 0.06 mm more than the actual gap setting. This is due to the mechanical tolerance of the roller bearings.

The gap setting and speed differential between the last two rolls determine the degree of refining and the control of the product temperature. Unlike plodders, which always increase the product temperature during refining, roll mills are capable of maintaining and even reducing the product temperature.

Soap pellets passing through a roll mill are usually converted into thin flakes that are then usually formed into “crimped flakes” for easier subsequent conveying. The flaker knife (take-off) is a blade designed with multiple cuts and angles to produce a thin flake. The crimped, compacted flakes are formed with a scraper blade and a crimping bar (Figure 8.7).

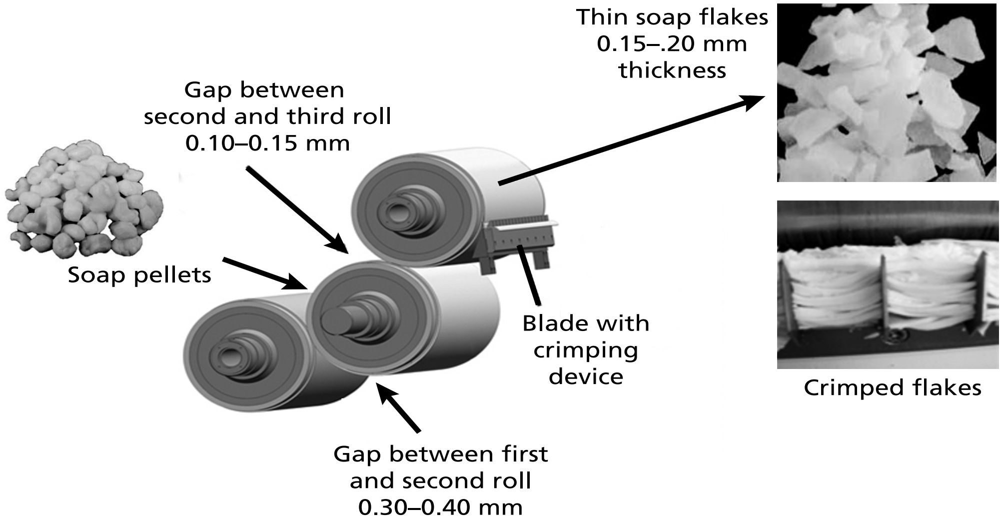


Figure 8.7 Roll mill refining.

Plodder and Roll Mill Refining Stages Comparison

A general comparison guide for the stages of refining using plodders and roll mills is presented in Table 8.3; the classification of finishing lines is based on the number of refining stages.

Table 8.3 Plodder and Roll Mill Refining Stages Comparison

Number of Refining Stages	Plodder Refining Screen Mesh Number	Roll Mill Flake Thickness (mm)
1½	80	0.15
1	50	0.20
¾	30	0.25
½	20	0.30
¼	10	0.40

Note: The use of finer than 50-mesh screens (such as 80-mesh) is not recommended due to an excessive product temperature rise and a potential production rate reduction.

Methods for Measuring the Degree of Refining

Washdown Temperature

The washdown-temperature test is used to measure the degree of refining by evaluating the presence of hard particles (specks) in soap feel (grittiness, sandiness, roughness). The bar is washed with both hands for 1 minute in a sink with 30 °C water. Once the bar surface is smooth and all protruding lettering and designs are washed away, the water temperature is decreased. Washdown temperature is the temperature at which one can detect the first hard specks.

- A smooth bar without any hard specks has a 22 °C washdown temperature.
- A slightly gritty feel appears at 23 to 24 °C.
- A moderately gritty feel appears at 25 to 26 °C.
- A gritty feel appears at 26 to 27 °C.
- A very gritty feel occurs when the washdown temperature reaches 28 °C or higher.

Photo-Evaluation Scale

One can also use a visual method for roughness evaluation. The bar is washed for 1 minute in 20 °C water and then left to dry. If the bar is held at an angle in front of a high-intensity light source and below eye level, one can easily see the dry specks. By using photographic standards, one can grade the bar as 0, 1, 2, 3, 4, or 5. Zero represents a smooth product and 5 is a very gritty bar (Figure 8.8).

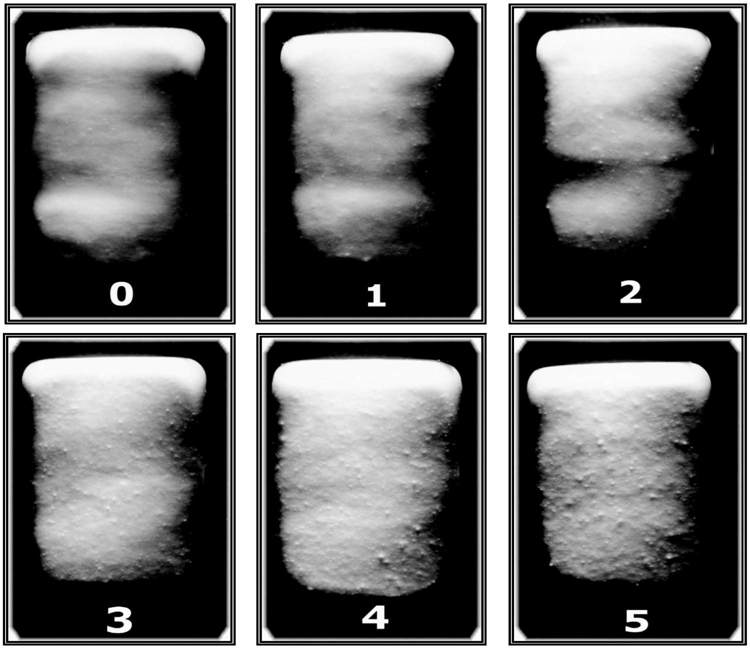


Figure 8.8 Photo-evaluation scale.

Prerefining

Pre-refining is a refining step performed before the addition of any minor liquid and solid additives to an old (fully aged) or to a new (fresh or partially aged) dry soap base. The use of a pre-refining step is especially advantageous for aged soap, low-moisture-content syndet, and high-titer soap. The main advantages of pre-refining are:

- Easier processing of hard, low-moisture-content syndet, high titer, and translucent soap.
- Better mixing of the liquid additives with the plasticized, higher temperature, partially refined base. This facilitates the refining action in the subsequent processing stages.
- Improved refining (lower washdown temperature of the finished product).

Soap Base Aging

If the soap base (with or without additives) is stored and aged before final refining, extrusion, and stamping, line efficiency increases considerably. During aging, soap crystallization is completed, and soap temperature is reduced. The optimal aging time has to be determined experimentally for each specific soap formula.

Finishing-Line Equipment

Mixers

Amalgamator with Open-Arm Sigma Blades

The most economical widely used mixer, called an *amalgamator* in the soap industry, is a top-loading, bottom-discharging, nontilting unit with two "open-arm type" sigma profile blades. This easy-to-clean, efficient blade design is derived from the sigma blade, which is the universal mixing blade in the chemical industry. These mixers mainly coat the outer surface of the pellets with the additives. Mixers only partially break up the pellets, thereby limiting the penetration of the additives (Figure 8.9).

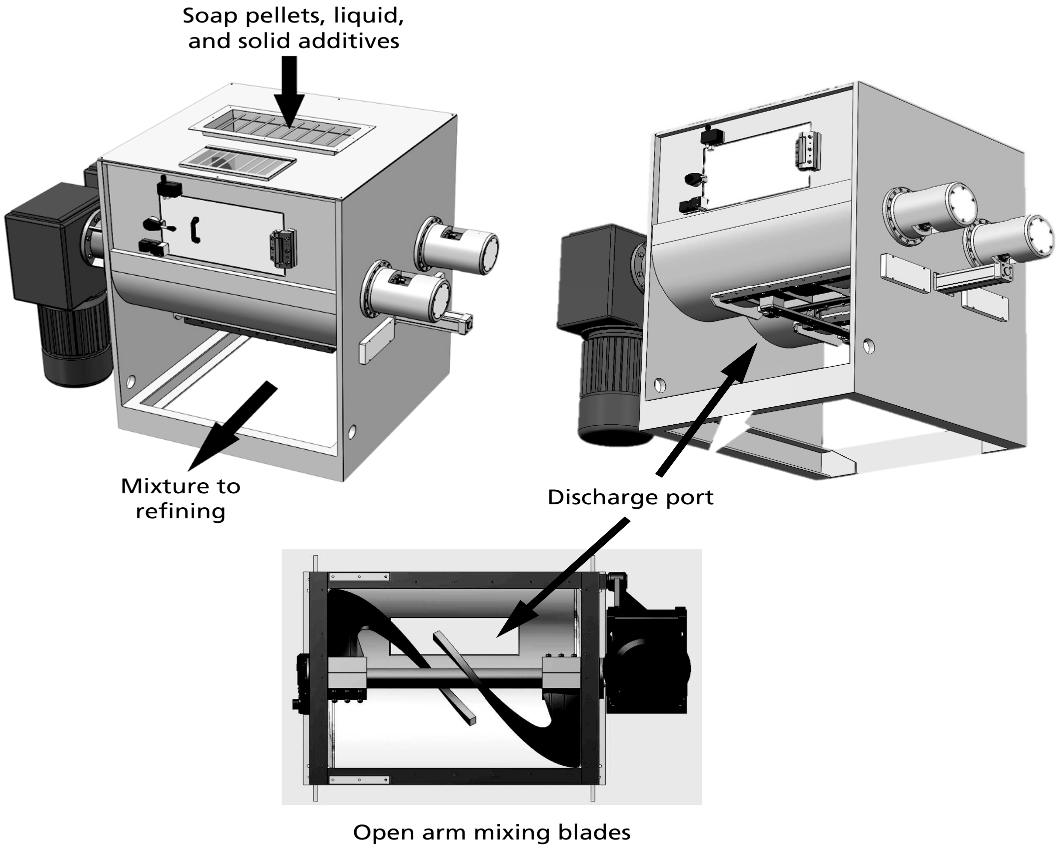


Figure 8.9 Amalgamator with open sigma blades (macro mixing).

Double-Arm Sigma Mixer

Double-arm mixers with two counter-rotating tangential sigma blades are very efficient units that have been widely accepted in the soap industry. They are applicable for all types of toilet, combo, syn–thetic and translucent soaps (Figure 8.10).

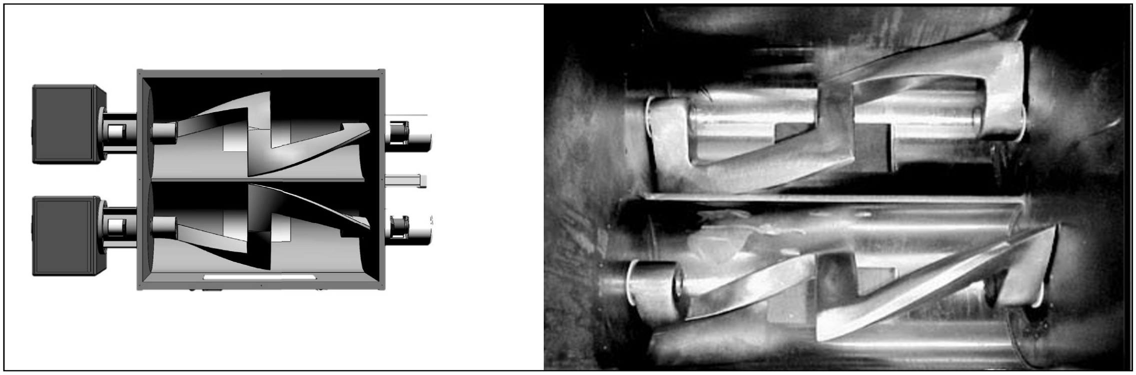


Figure 8.10 Double-arm sigma mixing blades.

Mixer-Kneader-Extruder

A mixer-kneader-extruder consists of two tangential counter-rotating sigma blades and a extruder-type discharge screw with a pelletizing head. During mixing, the blades rotate toward each other, creating intensive mixing/kneading action (Figure 8.11).

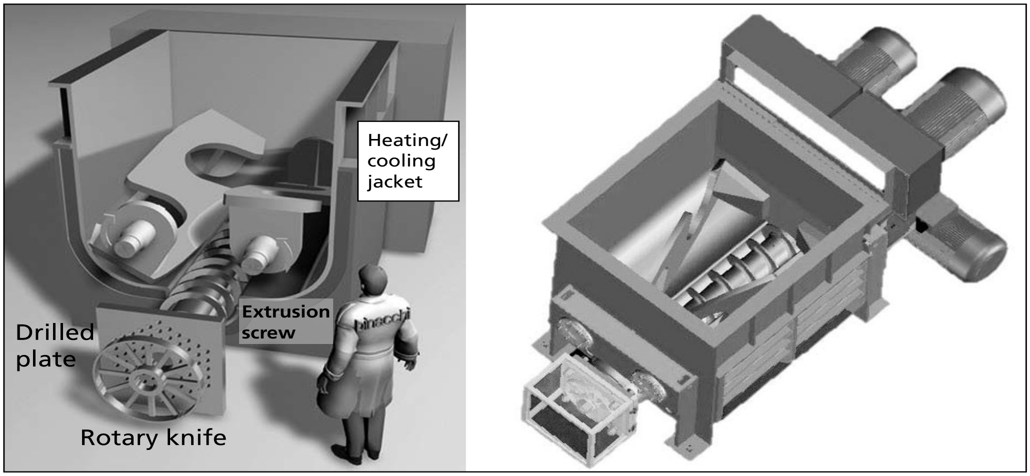


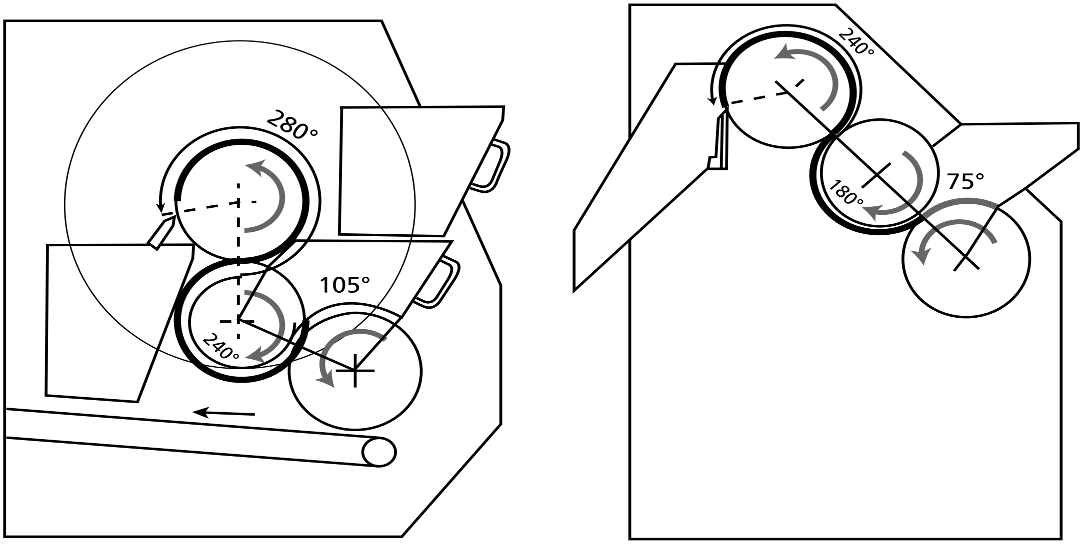
Figure 8.11 Mixer-kneader-extruder.
Source: Binacchi & Co.

The screw rotates in the reverse direction. At the end of the mixing cycle, the screw rotation is reversed to discharge and pelletize the mixture. The intensive mixing/kneading action by these units is especially suitable for combo, syndet, and translucent products.

Roll Mills

There are three-, four- and five-roll mill types for soap applications. Three-roll mills (Figures 8.12 and 8.13) are widely used for the following reasons:

- Lower operating costs due to lower power and cooling-water requirements.
- Large contact areas to ensure proper product refining and cooling.
- Easy gap-clearance-setting adjustment and control.
- Most of the total power absorbed, that is, the heat input to the soap, takes place between the last two rolls.



Mazzoni LB "L" shape
Configuration roll mill
Total contact area = 525°

Traditional design
Total contact area = 420°

Figure 8.12 Three-roll mill contact areas.

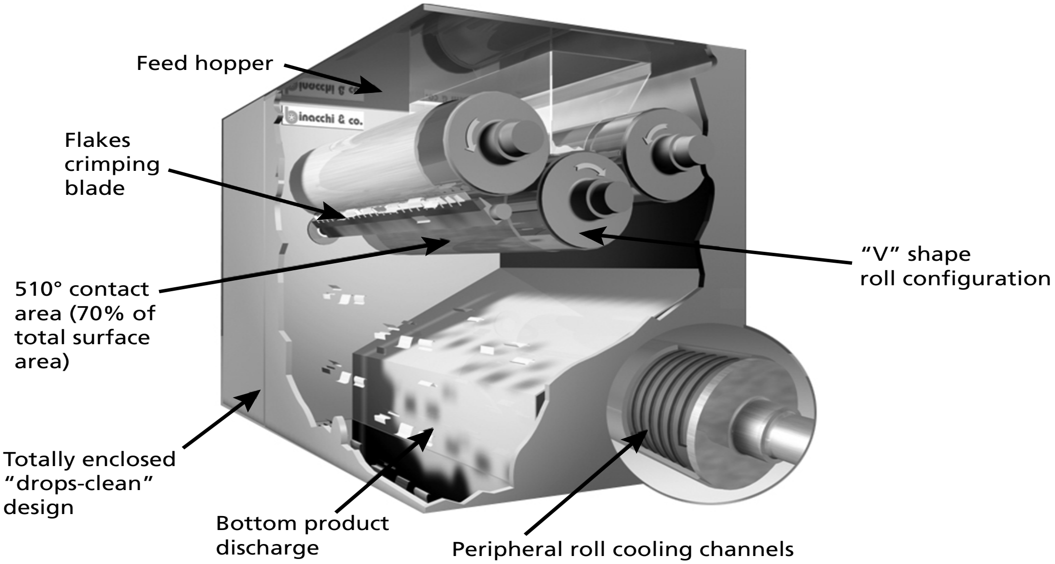


Figure 8.13 Binacchi BRM-V three-roll mill.
Source: Binacchi & Co.

Plodder Types

The soap industry uses three basic types of plodders, each of which is available in single-worm and twin-worm versions.

Simplex Refiners

A simplex refiner consists of one plodder designed to operate with a 50-mesh refining screen at a maximal pressure of 60 bar (Figure 8.14).

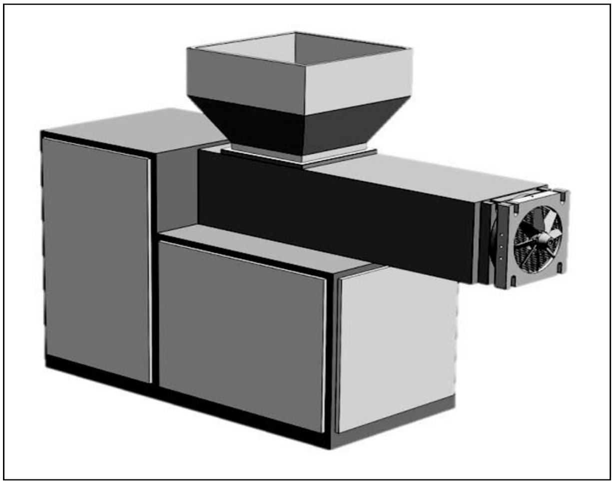


Figure 8.14 Simplex refiner.

Duplex Refiners

A duplex refiner consists of two simplex refiners mounted in tandem (Figure 8.15).

Duplex Vacuum Plodders

A duplex vacuum plodder consists of two plodders mounted in tandem and connected by a vacuum chamber (Figure 8.16). The preliminary stage plodder is exactly the same as a simplex refiner, and it can be used with a 50-mesh refining screen. In the final-stage plodder, the refined pellets are compacted and extruded as a continuous slug (billet) that does not have any entrapped air.

A plodder functions as a refiner when it is fitted with a 50-mesh screen. When 30- or 20-screens are used, the refining degree is reduced. The 10-mesh and coarser screens are used at times as backup, protective screens for the finer 30- or 50-mesh refining screens.

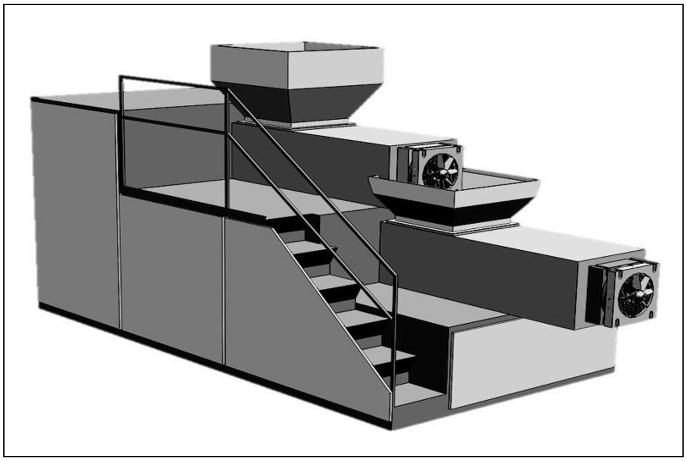


Figure 8.15 Duplex refiner.

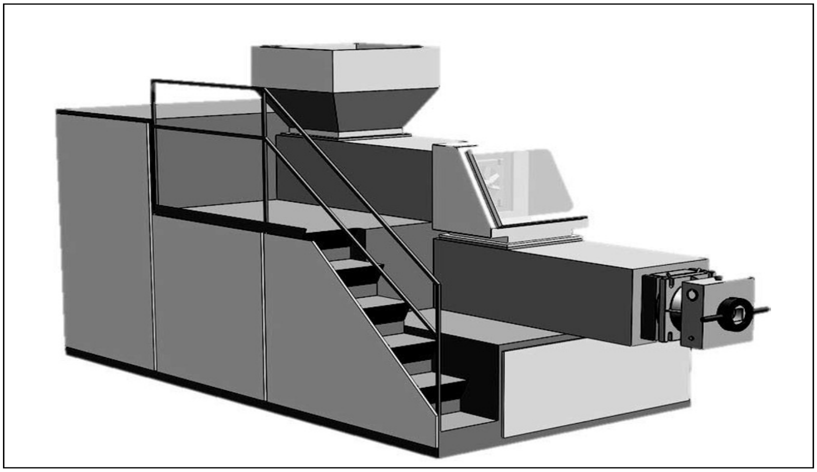


Figure 8.16 Duplex vacuum plodder.

Triplex Plodder (TP)

A triplex plodder consists of a simplex refiner positioned at a right angle above a duplex vacuum plodder (Figures 8.17.)

The advantages of using a triplex plodder in a finishing line are:

- Shorter overall length
- Only one main belt conveyor between the mixer and the simplex refiner
- Short in-line recycle conveyor into the simplex refiner
- Bypassing the simplex refiner option, using only the duplex vacuum plodder for white soaps with a small quantity of additives

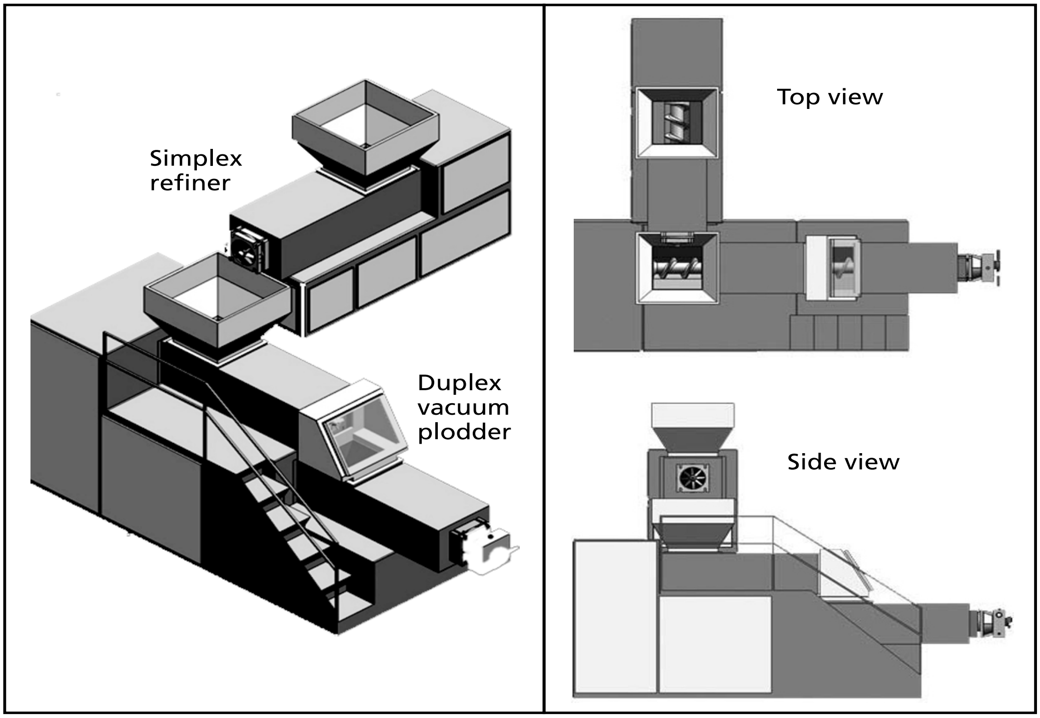


Figure 8.17 Triplex plodder (TP).

Plodder Refining and Pelletizing Group

The refining stage of any plodder has a refining and pelletizing group as shown in Figure 8.18. Further details are shown in Figure 8.19.

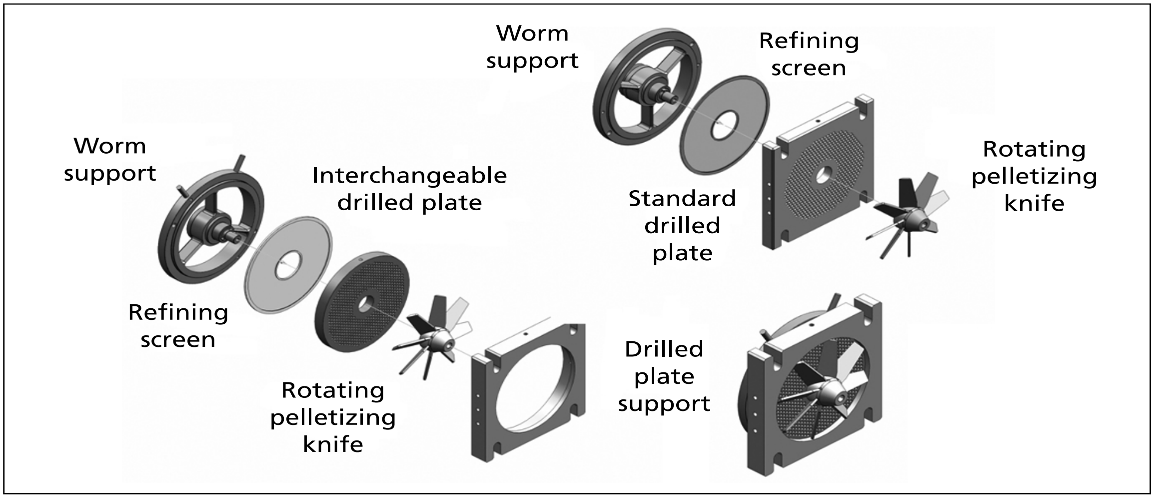


Figure 8.18 Plodder refining and pelletizing group.

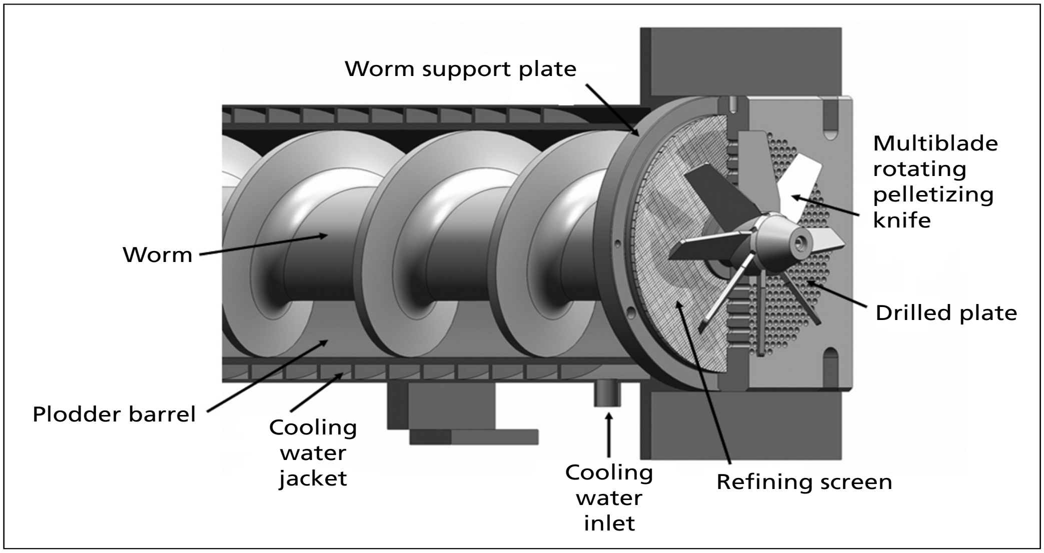


Figure 8.19 Refining/pelletizing stage details.

Plodder Extrusion Group

All of the components of the extrusion group of a duplex vacuum plodder are illustrated in Figure 8.20.

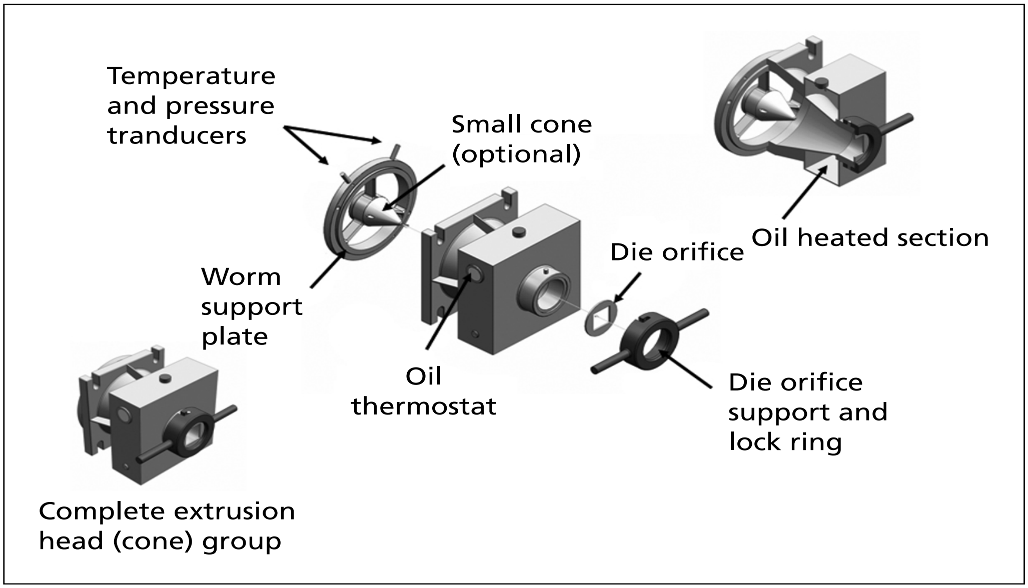


Figure 8.20 Plodder extrusion group.

Plodder Worms

Plodder worms are designed to perform refining, compression, and extrusion functions.

Worm Types

There are three types of plodder worms:

1. Single worm
2. Tangential twin-worm
3. Nontangential twin-worm

Twin-worm plodders are available with tangential (touching) counter-rotating worms in a single barrel or nontangential (nontouching) counter-rotating worms in two separate barrels. Twin-worm plodders with tangential counter-rotating worms in a single barrel are recommended for processing sticky products and for high-capacity production lines.

Nontangential twin-worm plodders are used for high-speed lines and multicolored soaps.

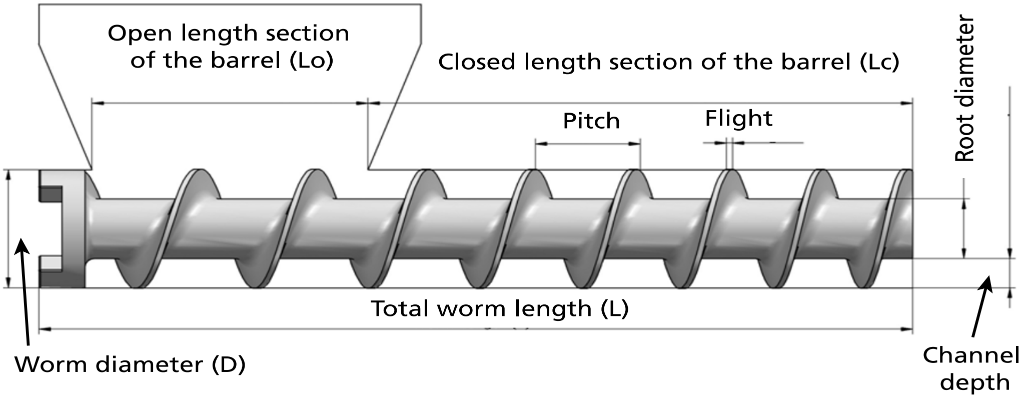


Figure 8.21 Plodder worm details.

Abbreviations: Total worm length (L); length of the closed section of the barrel (Lc); worm diameter (D).

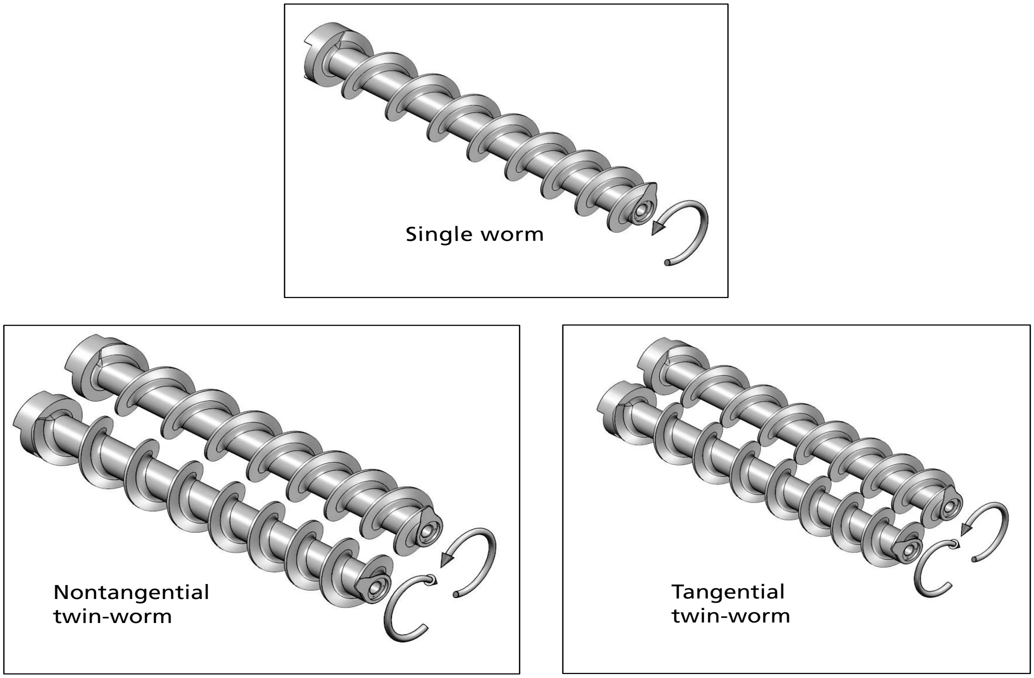


Figure 8.22 Plodder worm styles.

Worm Styles

Several worm styles are available with different profiles suitable for various applications. Binacchi & Co., Mazzoni LB, and Soaptec worms are shown in Figures 8.23, 8.24, and 8.25.

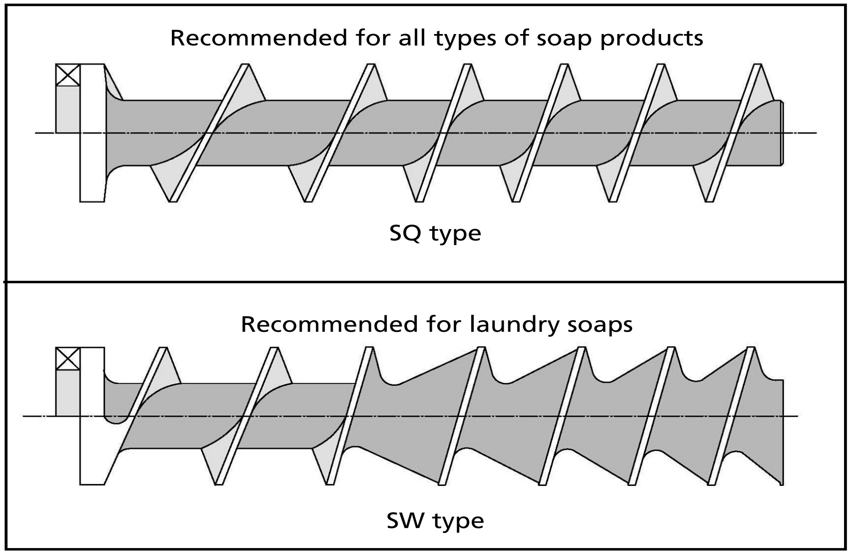


Figure 8.23 4:1 Lc/D ratio plodder worms.
Source: Binacchi & Co.

3:1 L/D for standard plodders		
High volume (HV) For large capacity toilet and laundry soap dryers		Increasing root diameter Decreasing pitch
4:1 L/D for standard plodders		
High efficiency (HE) For all types of products		Constant root diameter Decreasing pitch
Constant (CT) For products requiring reduced mechanical work		Constant root diameter Constant pitch
7:1 L/D + 2:1 L/D for MRP plodders		
High efficiency long (HEL) For all types of products		Constant root diameter Decreasing pitch

Figure 8.24 Mazzoni LB plodder worms.
Source: Mazzoni LB, SpA.

Universal type with decreasing pitch	Double spiral high shear type
	

Figure 8.25 Soaptec 4:1 Lc/D ratio plodder worms.
Source: Soaptec.

Short- and Long-Lc/D Ratio Plodders

The old conventional plodders had 3:1 Lc/D ratios and operated at 12–15 rpm worm speeds. In 1986, G. Mazzoni SpA introduced the NOVA 5:1 Lc/D ratio plodders, which operated at 18–20 rpm worm speed. Currently all suppliers offer 4:1 Lc/D-ratio plodders. In 1992 the NOVA series was replacede by the HE 4:1 Lc/D ratio plodders.

Long-Lc/D Ratio Plodders with Special Worms and Refining Devices

Mazzoni LB Multi-Refining Plodder

The multi-refining plodder (MRP) is a duplex vacuum plodder. The MRP's first stage is refining, which has a 4:1 Lc/D ratio HE twin-worm plodder. The final stage is multi-refining and extrusion, which has a single-worm plodder in two separate sections.

The first section has a 7:1 Lc/D ratio HEL worm and the second section—a refining stage extension—has a 2:1 Lc/D ratio worm (Figures 8.26 and 8.27).

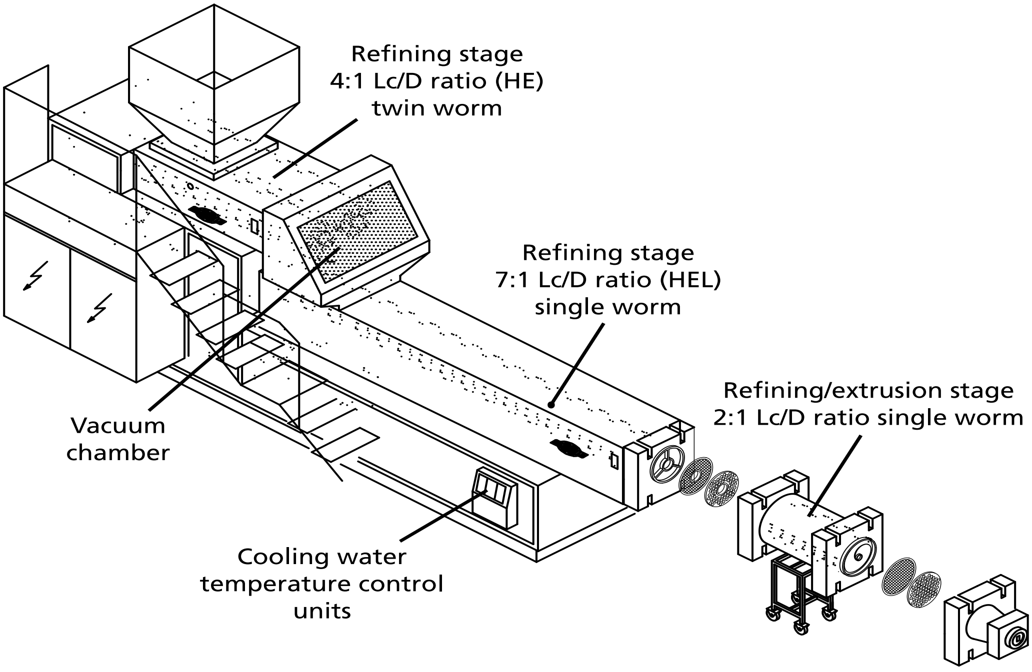


Figure 8.26 Mazzoni LB multi-refining plodder (MRP).
Source: Mazzoni LB, SpA.

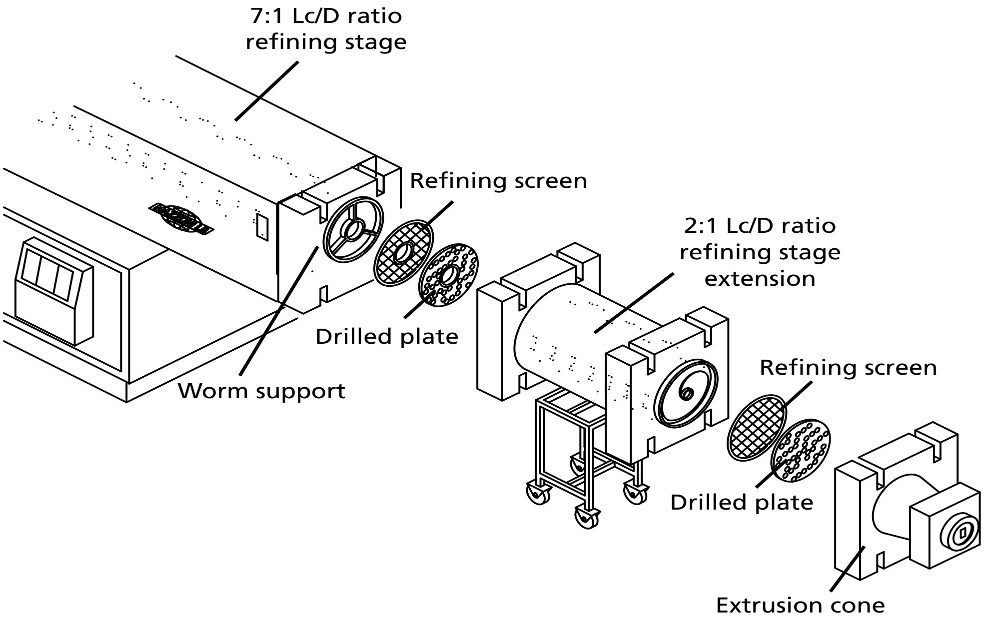


Figure 8.27 Mazzoni LB multi-refining plodder (MRP) final stage.
Source: Mazzoni LB, SpA.

SAS "Flexi" Plodder

Flexi plodders are available as:

- Simples refiners with two refining sections in one plodder
- Duplex vacuum plodders totalling three refining sections plus an extrusion section or in a combination of a conventional refining stage together with a Flexi stage (Figures 8.28 and 8.29).

The SAS Flexi plodders feature two special components:

- A combo-screw (Figure 8.30, page 188)
- A "shearing plates group (Figure 8.31, page 188)

The long 8:1 L/D ratio combo-screw allows the soap to reach high—up to 100 bar—working pressure in the last section of the barrel, allowing the use of refining screens and shearing plates. This results in having practically double refining per stage.

The shearing plates group consists of a fixed plate, and and adjustable (movable) plate embedded inside the fixed plate. The position of this plate determines the quantity of soap passage, working pressures, and degree of refining required for each type of soap formulation.

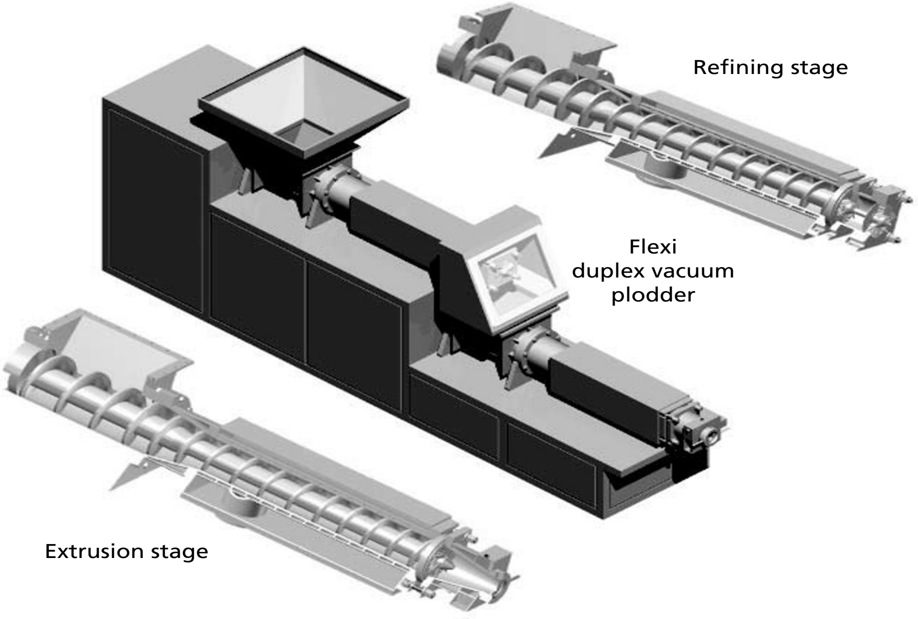


Figure 8.28 SAS Flexi duplex vacuum plodder.

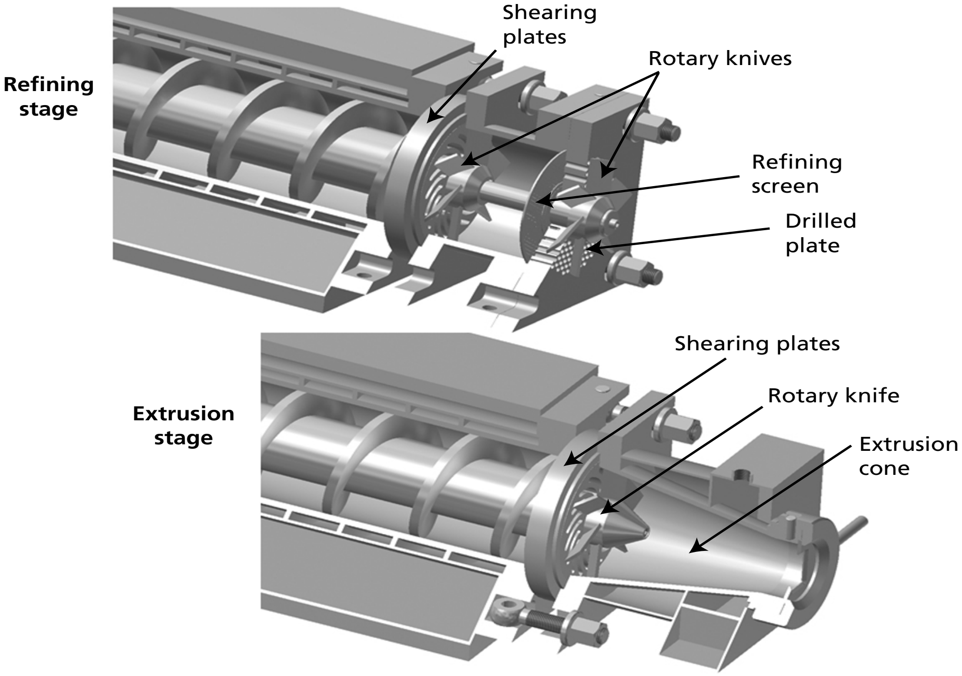


Figure 8.29 SAS Flexi plodder details.

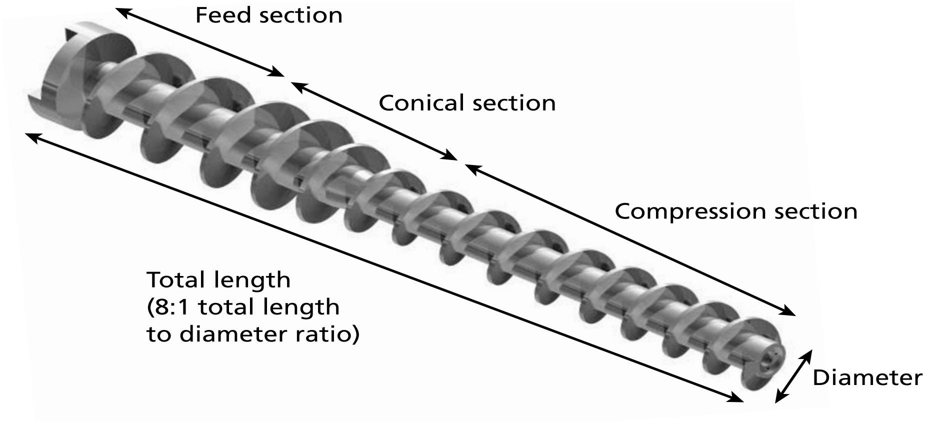


Figure 8.30 SAS combo-screw.

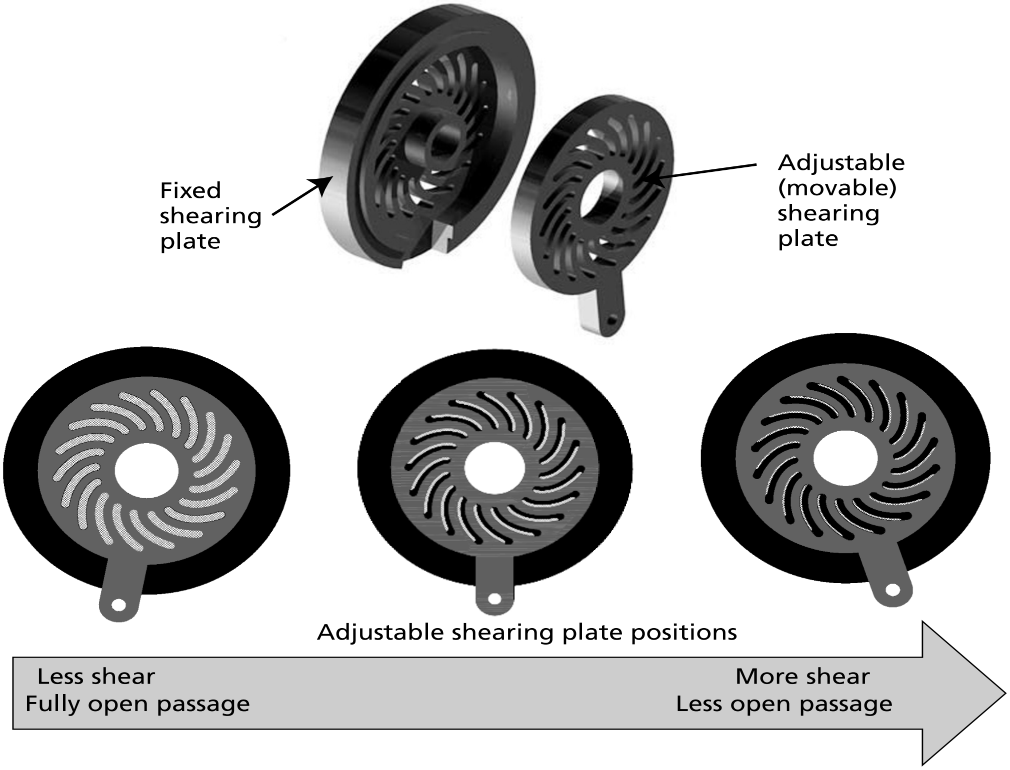


Figure 8.31 Shearing plates group.
Source: SAS.

Cutters

Soap is extruded from the duplex vacuum plodder as a continuous slug (billet) in a shape determined by an extrusion die plate. Presses with traditional stamping systems require single slugs of predetermined length. All the current generations of presses operate in the “flashstamping” mode that requires the use of long, multiple-length slugs. The mechanical multiblade cutters with fixed and manually adjustable chains have been replaced by high cutting precision and high-speed electronic cutters. These cutters can cut single length, long multilength, and short length for recycle mode slugs. The application of engraving rollers with these cutters is growing as an economical alternative to stamping. Engraving can be on two horizontal, two vertical, or all four sides of the slug. A few units are illustrated in Figures 8.32 through 8.35.

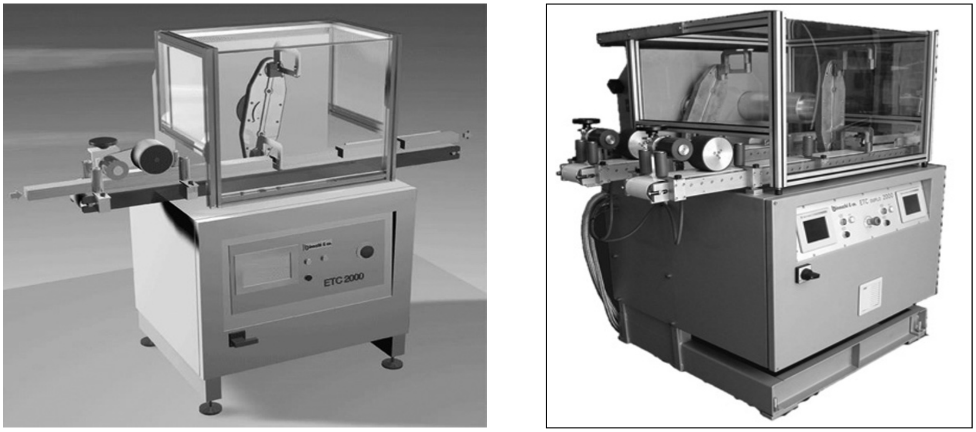


Figure 8.32 Binacchi “ETC-2000” double-blade toilet soap electronic cutter.
Source: Binacchi & Co.

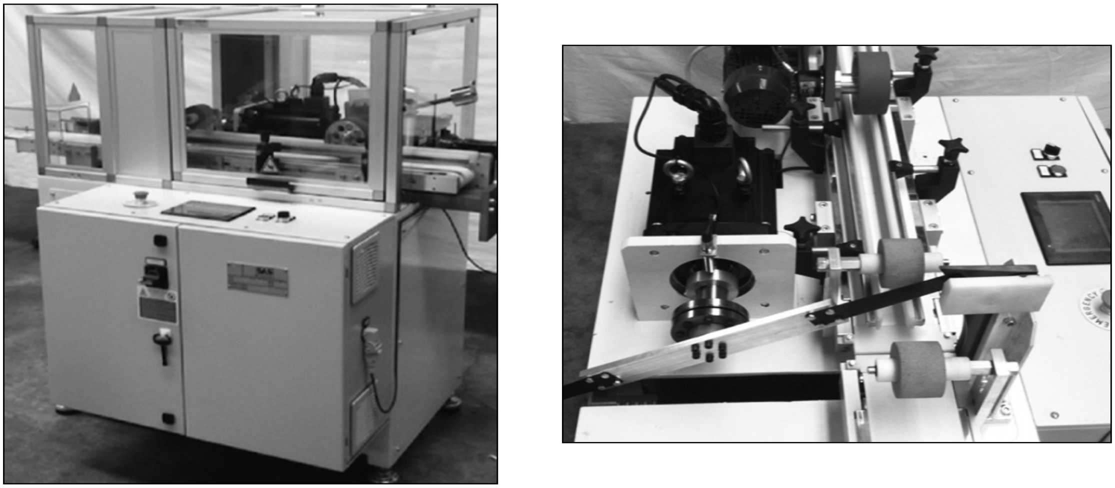


Figure 8.33 SAS Easycut two-blade electronic cutter.
Source: SAS.

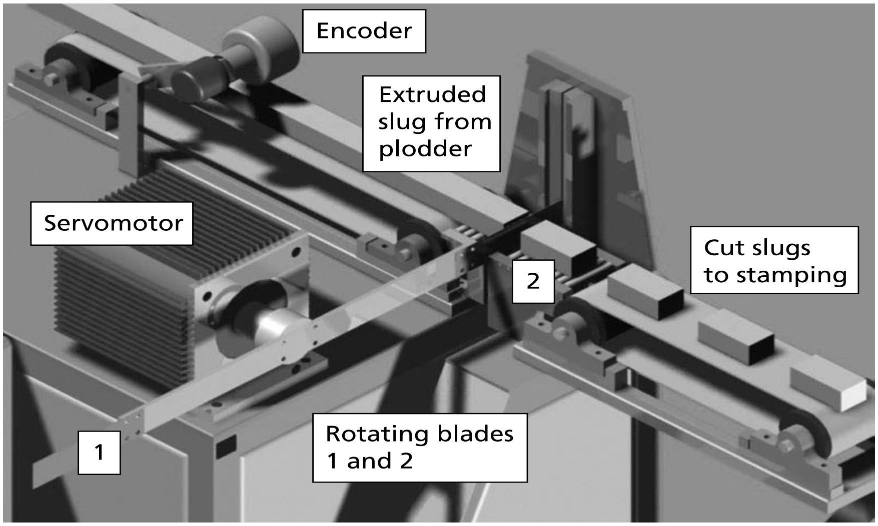


Figure 8.34 SAS Easycut two-blade electronic cutter.
Source: SAS.

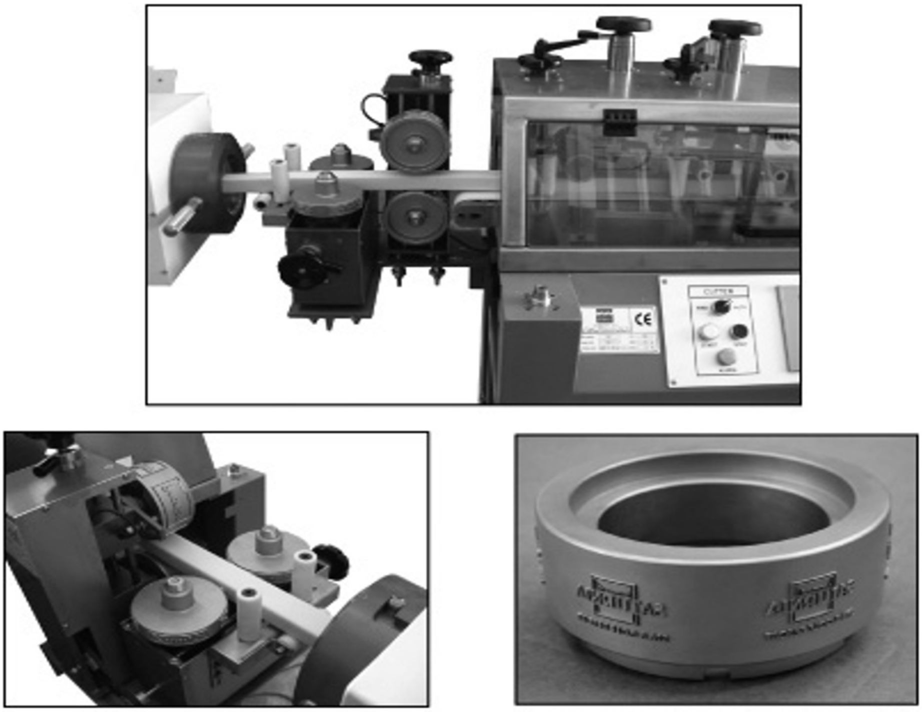


Figure 8.35 Soaptec electronic cutter with engraver rolls.
Source: Soaptec.

Presses

Soap Shapes

The following two basic shapes of soap exist:

1. Banded (with a side band)—all soap shapes with vertical sides as their periphery
2. Bandless (without a side band)—all soap shapes with only one parting line, that is, without vertical sides around their circumference.

One can further classify all banded and bandless shapes into four variations: rectangular, round, oval, and irregular (Figure 8.36).

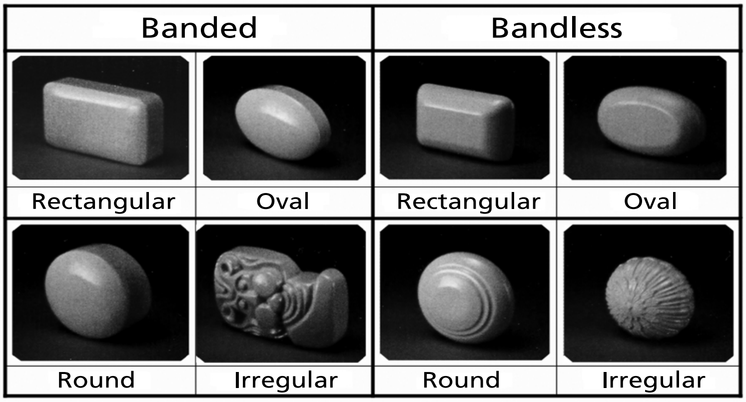


Figure 8.36 Soap shapes.

Soap Presses

Flashstamping-type soap presses use only dies and corresponding counter-dies to stamp all banded, bandless, and specialty shaped products.

"Flashing" is the excess soap formed around the periphery of the dies as the dies meet, forming the final bar shape and setting the stamped bar weight.

Flashstamping requires a 10–30% heavier slug weight than the final stamped bar weight. This extra weight requirement must be taken into account to properly size the extrusion rate of the final plodder.

Soap presses utilizing the traditional die-box stamping system are in limited use due to stamping speed and soap-shape stamping limitations.

Vertical and Horizontal Motion Flashstamping Soap Presses

Mazzoni LB's vertical motion flashstamping STUR presses have been on the market since 1989 (Figure 8.37). Binacchi's model USN-500 horizontal motion flashstamping press, introduced in 1989, was the first dual mandril press designed to accommodate up to eight dies (four on each mandril). One set was mounted on a reciprocating die slide, and the other two sets were mounted on a 180° rotating mandril.

The USN-2000 Series presses introduced in 2006 are vertical motion units with one-third fewer dies, since they do not have rotating mandrils.

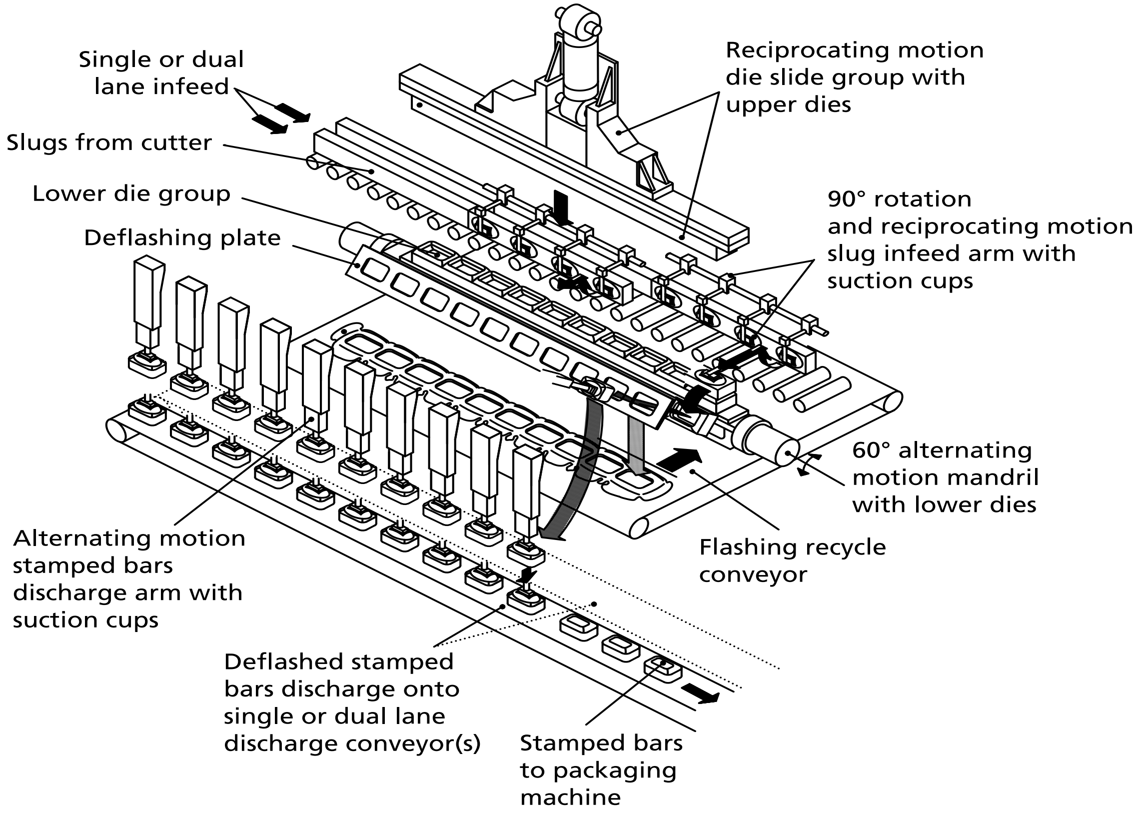


Figure 8.37 Mazzoni LB STUR flashstamping soap press.
Source: Mazzoni LB, SpA.

Direct Noncontact Bar Soap Transfers for Cartoners and Wrappers Interface

Binacchi Direct Product Transfer (DPT)

In 1989, Binacchi introduced a noncontact bar soap transfer as an integral part of their model USN-500 soap press coupled to a soap cartoner. This invention broke the then-prevailing maximum 300 cartons per minute speed barrier.

Six years later, the DTP system was offered for the direct interface with Binacchi soap wrappers. The application of the DPT has been growing steadily because it allows high-speed soap packaging operations.

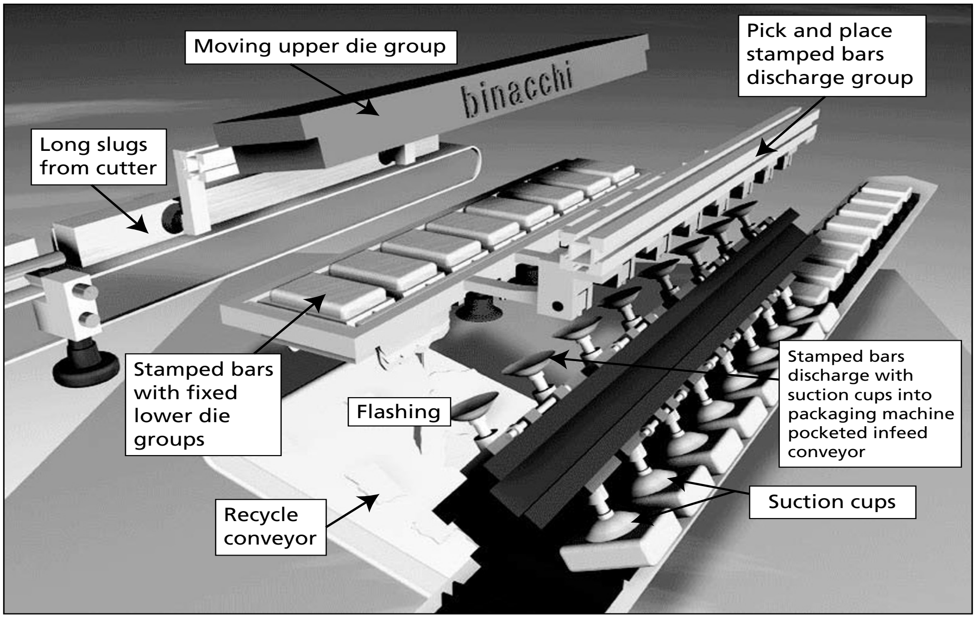


Figure 8.38 Binacchi USN presses with direct transfer group (DPT) for packaging machinery integration.
Source: Binacchi & Co.

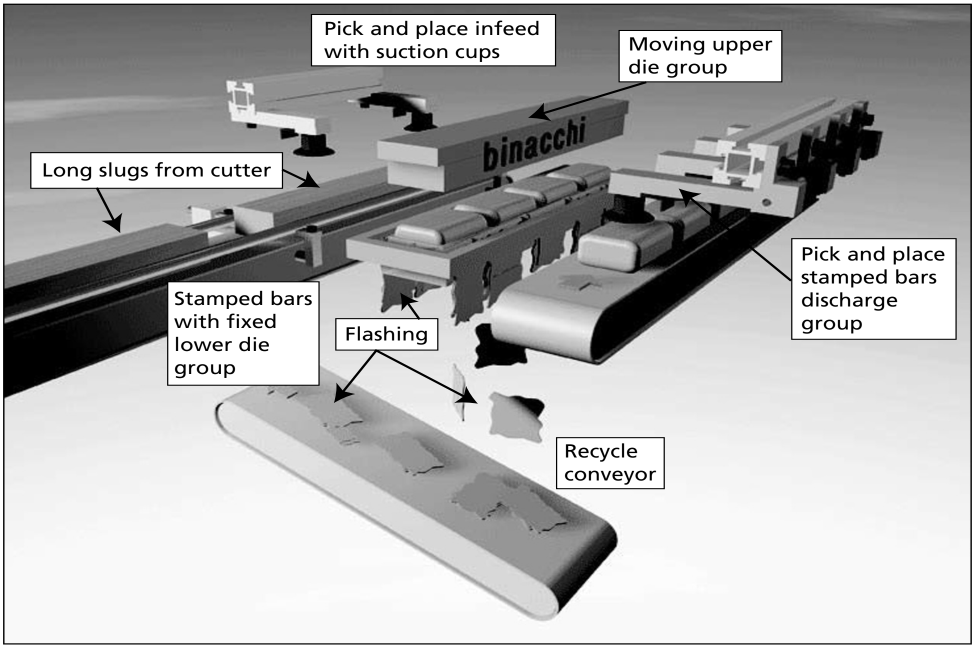


Figure 8.39 Binacchi USN-2000 soap presses stamping system.
Source: Binacchi & Co.

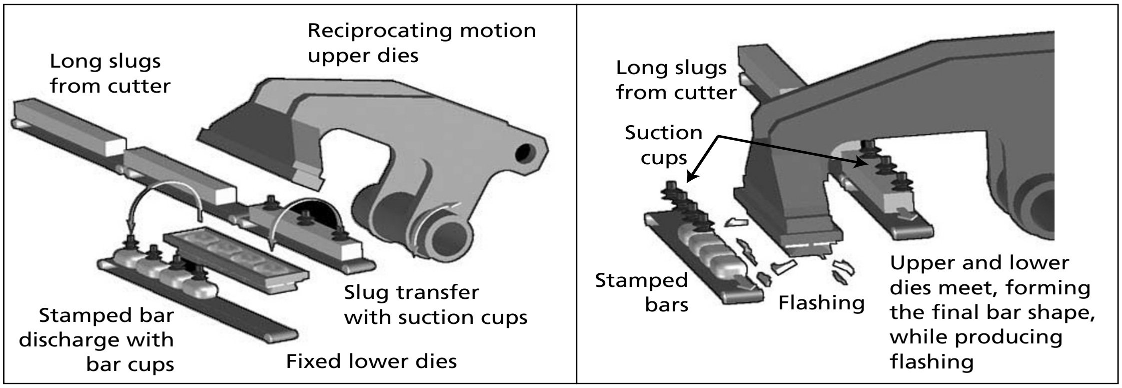


Figure 8.40 Binacchi flashstamping soap press system.
Source: of Binacchi & Co.

Mazzoni LB Direct Transfer System (DTS)

The Mazzoni LB direct transfer system (DTS) was introduced in 2006. A set of vacuum transfer cups rotates, spaces in pitch, and places the stamped bars by using a single-step rotation into the pocketed infeed conveyor of the packaging machines (Figure 8.41).

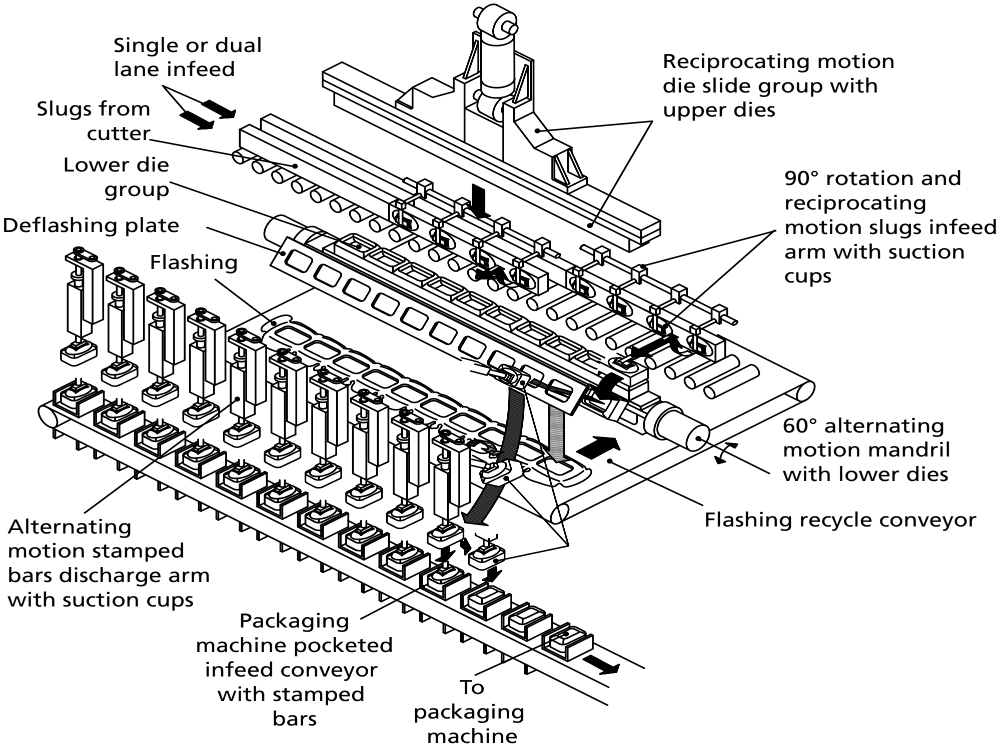


Figure 8.41 Mazzoni LB STUR flashstamping soap press with DTS system.
Source: Mazzoni LB, SpA.

High-Speed Presses and Packaging Machinery

High-speed soap press wrappers, cartoners, and flow wrappers for bar soaps are summarized in Tables 8.4, 8.5, and 8.6.

Table 8.4 Binacchi High-Speed Soap Presses and Packaging Machinery

Press Model	Number of Dies	Stamped Bars per Minute	Wrapper Model		Cartoner Model		Flow Wrapper Model	
			Model	Speed	Model	Speed	Model	Speed
USN-2350E	8	400	BSW-400	400	BSC-400/400	400	BFP-400/400	400
USN-2650E	12	600	BSW-555	500	BSC-500/500	500	Two BFP-400	300 + 300
USN-2750E	16	800	Two BSW-400	400 + 400	Two BSC-400	400 + 400	Two BFP-400	400 + 400
USN-2750E	18	900	Two BSW-550	450 + 450	Two BSC-500	450 + 450	Two BFP-500	450 + 450

Note: Data based on 100 grams stamped bar weight.

Table 8.5 Mazzoni LB High-Speed Soap Presses and Packaging Machinery

Press Model	Number of Dies	Stamped Bars per Minute	Stamped Bar Weight (Grams)	Wrapper Model	Cartoner Model	Flow Wrapper Model
STUR-8	6	360	150–200	ACMA 7350/771	ACMA 330	MLB500
STUR-8/DTS	7	420	150	ACMA 771DL	ACMA 770DL	MLB50/DL
	8	480	100			
	8	480	150–200	ACMA 771	ACMA 770	MLB500
STUR-10	10	600	100–150	Two ACMA 7350		Two MLB500
	12	720	75–100			
	8	480	150–200	ACMA 771	ACMA 770	MLB500
STUR-12	10	600	100–150	Two ACMA 7350		Two MLB500
	12	720	100			
STUR-12 DST/120	10	600	100–150	—	ACMA 770/DL	MLB500/DL
STUR-ULTRA	10	600	200–250	Two ACMA 7350	Two ACMA 330	Two MLB500
	12	720	150–200	Two ACMA 771	Two ACMA 770	
	14	840	100–150			
	16	960	75–100			
STUR-ULTRA DTS-144	12	720	75–200	ACMA 771/DL	—	—
STUR-ULTRA DTS-180	10	550	75–200	ACMA 771/DL	—	—

Abbreviations: Direct transfer systems used with the ACMA/GD soap packaging machine (DTS); ACMA/GD soap packaging machines (ACMA); Mazzoni LB soap packaging machines (MLB).

Note: Packaging speeds are not listed. Actual speeds depend on soap product type, bar shapes, and weight.

Table 8.6 SAS High-Speed Soap Presses and Packaging Machinery

Press Model	Number of Dies	Stamped Bars per Minute	Wrapper Model	Wrapper Speed	Flow Wrapper Model	Flow Wrapper Speed
STAMPEX/4	4	280	WRAPPEX	220	ZA-230	250
STAMPEX/6	6	400–450			ZA-360	360
STAMPEX/8	8–10	500–600				
STAMPEX/10	10–12	600–720				

Note: Stamped bar weights range from 100 to 200 grams.

Water Chillers for Plodders and Roll Mills

Water chillers are designed to circulate clean, chilled water to plodders and roll mills in a closed circuit. Chilled water ranging in temperature from approximately 8 °C to 15 °C circulates in the barrels of plodders and in the rolls of roll mills. The exact operating temperature depends on the product and the processing role.

The initial investment in and operating cost of chillers are offset by the cost of non-recycled cooling water, varying seasonal water-temperature limitations, elimination of periodic maintenance required to remove hard-water deposits, and ability to use the optimal chilled water temperature for the given process.

Low-Temperature Glycol/Water Chillers for Soap Press Dies

Low-temperature glycol chillers are designed to supply a glycol/water coolant solution at –30 °C to soap press dies. The cooling capacity of packaged chillers is expressed in tons; however, the actual capacity varies with process temperatures and ambient temperatures. For example, a unit rated for about 5,000 Kcal/hour at –30 °C would provide 8,000 Kcal/hour at –20 °C; 11,000 Kcal/hour at –10 °C; and 17,000 Kcal/hour at 0 °C. As another example, with nominal cooling capacity at 28 °C ambient temperature, the cooling capacity would decrease by about 12% if the ambient temperature increased to 38 °C.

Chiller Sizing

Chiller sizing is calculated by the following formula:

$$\text{Tons of refrigeration} = \text{GPM} \times \Delta T/24 \qquad \text{(Eq. 8.1)}$$

where GPM is the water flow rate in gallons per minute and ΔT is the temperature differential in °F between the water leaving and entering the system.

The design capacities are also based on an ambient air temperature of 35 °C for air-cooled chillers and a 30 °C condenser water temperature for water-cooled chillers. As a rule of thumb, the cooling capacity of a chiller is reduced by 2% for each 0.5 °C below 10 °C.

Cooling Systems for Plodders, Roll Mills, and Soap Press Dies

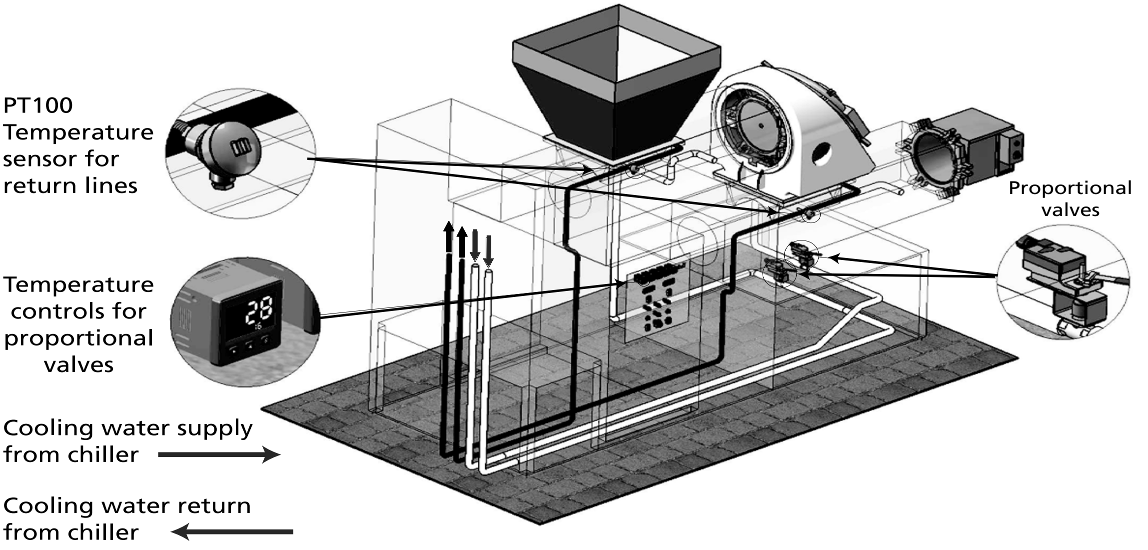


Figure 8.42 Cooling water control system for plodder jackets.
Duplex plodder application is illustrated courtesy of HADA S.A.

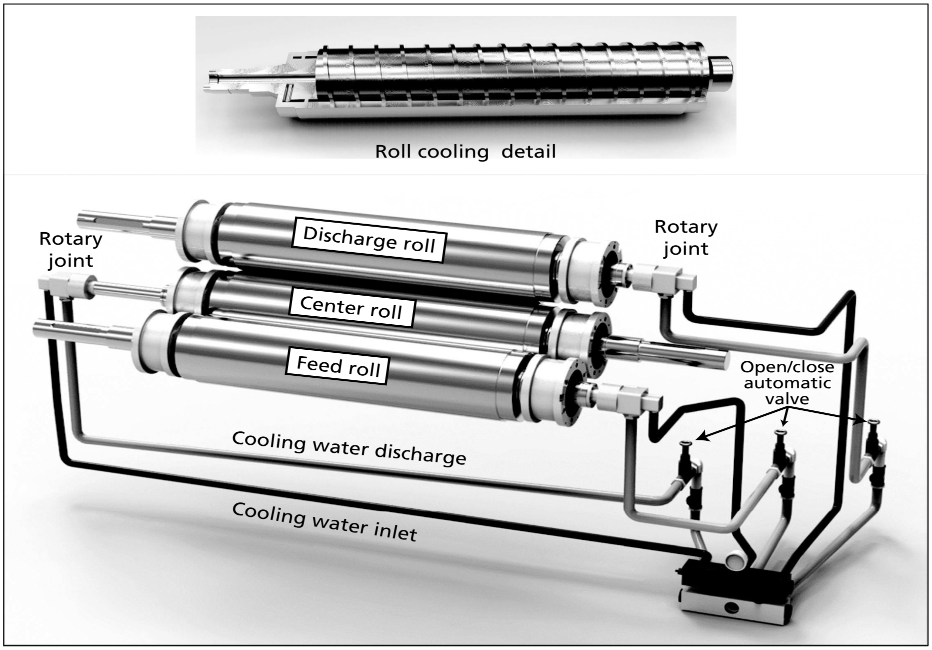


Figure 8.43 Three-roll mill cooling water system.
Source: Soaptec.

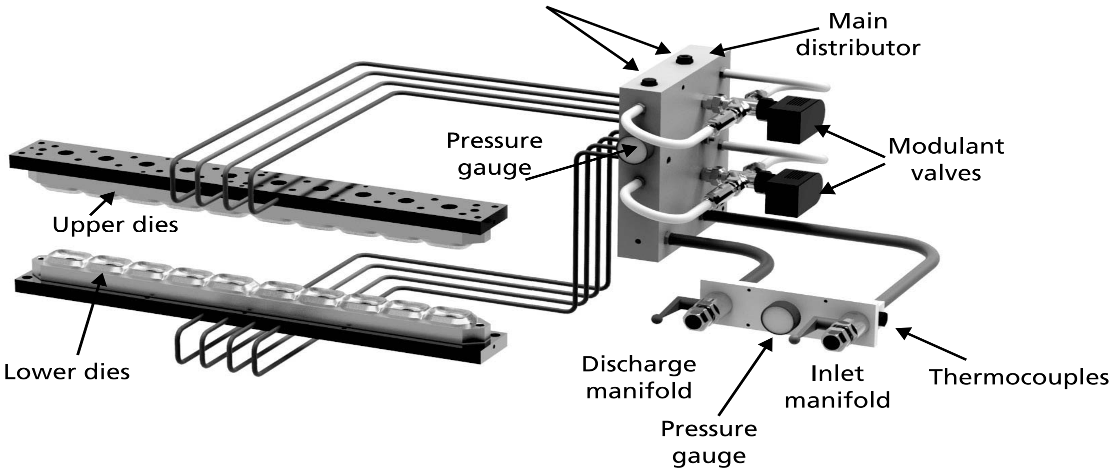


Figure 8.44 Soap press die set cooling system.
Source: Soaptec.

Cooling units are rated in tons of refrigeration, which measure the cooling effect of 2,000 pounds (a short ton) of ice melting in 24 hours. This turns out to be 288,000 heat units in 24 hours, or 12,000 heat units per hour. For the cooling capacity of water, note:

- In the United States: 1 ton = 12,000 Btu/hour = 3,024 Kcal/hour
- In Great Britain: 1 ton = 14,256 Btu/hour = 3,592 Kcal/hour
- In Europe: 1 frigorie/hour = 756 Kcal/hour = 3,000 Btu/hour

Chiller capacities in the United States are based on a flow rate of 2.4 gallons per minute per ton and a temperature drop of 10 °F.

Soap Finishing Line Types and Selection

The selection of a bar soap finishing line depends on the following:

- Types of products to be produced
- Line operating speed
- Number of refining stages required
- Choice of an all-plodder or a combination plodder and roll-mill line
- Rework/recycle quantity and recycle location
- Multifunction line layout

The three most widely used lines in various layout configurations are:

1. Line with three plodders (two refining stages)
   A simplex refiner and a duplex vacuum plodder (Figure 8.45)
2. Line with four plodders (four refining stages)
   A duplex refiner and a duplex vacuum plodder (Figure 8.46).
3. Line with three plodders and one roll mill (three refining stages)
   A simplex refiner a three roll mill and a duplex bacuum plodder (Figure 8.47).

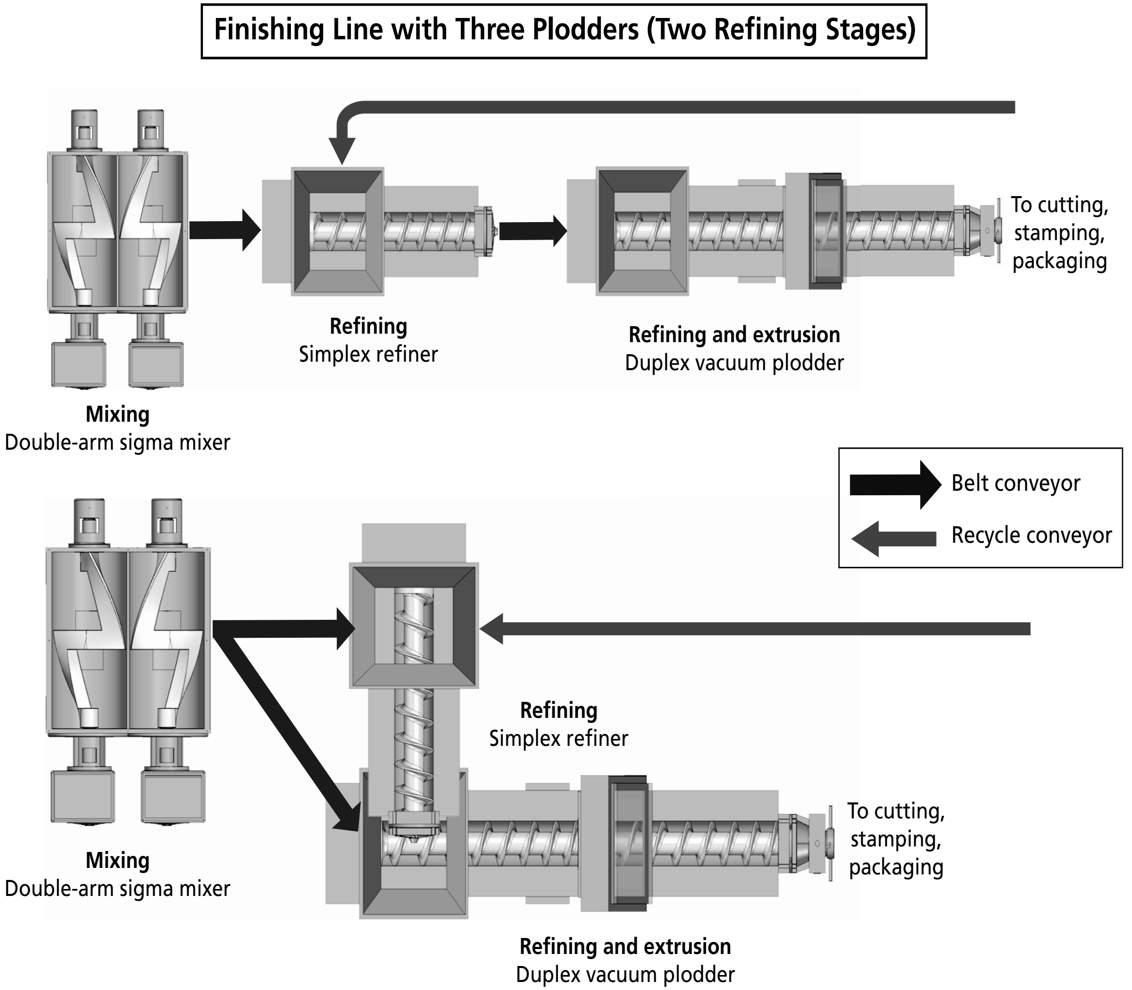


Figure 8.45 Finishing line with three plodders (two refining stages).

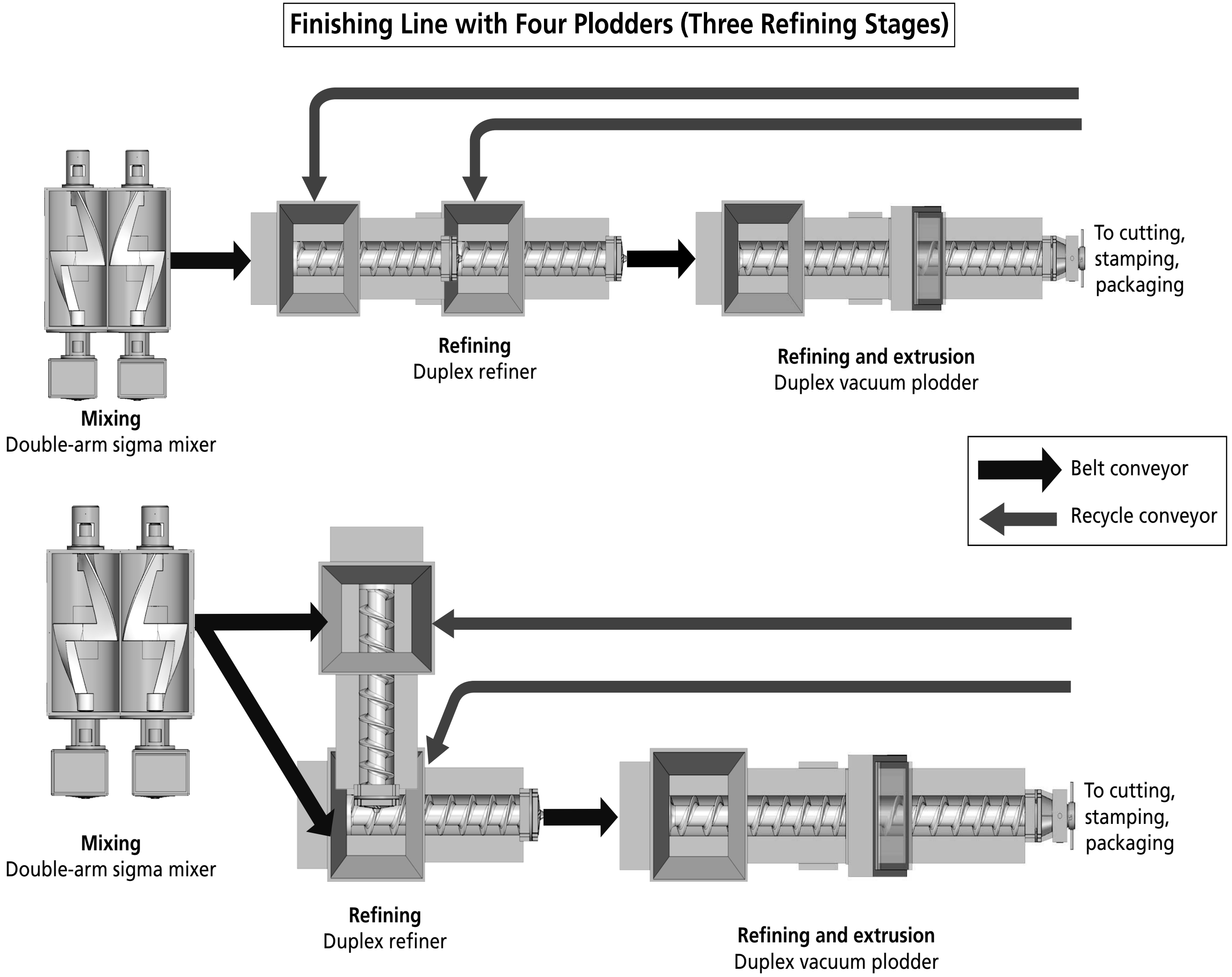


Figure 8.46 Finishing line with four plodders (three refining stages).

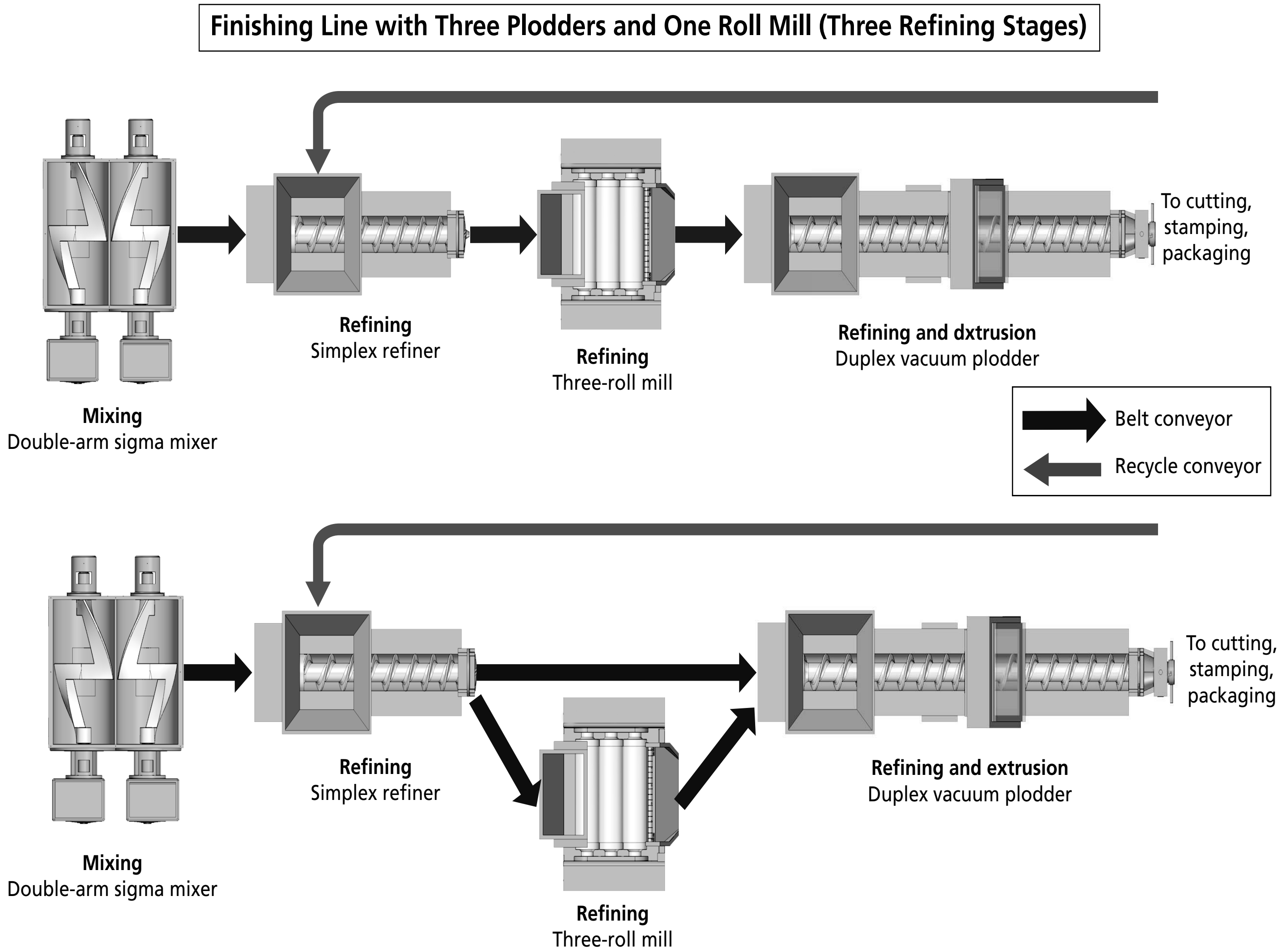


Figure 8.47 Finishing line with three plodders and one roll mill (three refining stages).

Single and Dual Purpose Line Layouts

Each line is illustrated in two configurations, in-line and right-angle (Figures 8.45–8.47). In a standard in-line layout, the product passes from one machine to another without the option of bypassing one unit.

For some products, less refining (less mechanical work) is required. The dual-function right angle layout option is shown for each line.

Table 8.7 Finishing Lines Selection Guide—Capacity (Kg/h), Speed (Bars/Minute), Bar Weight (Grams)

	85 grams		100 grams		150 grams		200 grams	
Bars per Minute (BPM)	**Stamped Bars (Kg/h)**	**Extruded Soap (Kg/h)***	**Stamped Bars (Kg/h)**	**Extruded Soap (Kg/h)**	**Stamped Bars (Kg/h)**	**Extruded Soap (Kg/h)**	**Stamped Bars (Kg/h)**	**Extruded Soap (Kg/h)**
100	510	640	600	750	900	1150	1200	1500
200	1020	1280	1200	1500	1800	2300	2400	3000
350	1765	2250	2100	2625	3150	4015	4200	5250
400	2040	2560	2400	3000	3600	4600	4800	6000
550	2800	3520	3300	4125	4950	6325	6600	8260
600	3060	3800	3600	4600	4500	5600	7200	9000

*Amount of extruded soap from the final plodder in Kg/h, assuming 25% flashing. Flashing can vary from 15% to 35% depending on the final stamped bar shape.

Acknowledgments

I appreciate very much the information and illustrations provided by Binacchi & Co., Mazzoni LB SpA, SAS Mariani Srl, and Soaptec Srl.

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9 Soap, Soap/Synthetic, and Synthetic Laundry Bars

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Introduction

Bar soap for washing clothes was the product most used in the world until the appearance of powdered detergents in the 1950s. The first laundry bars were mottled blue soaps introduced in Germany in the mid-1800s. Later they became popular in France, Spain, and Italy. Procter & Gamble offered a mottled German laundry soap in 1868.

In 1889, Lever Brothers Company registered the trademark name *Sunlight* in all countries (Figure 9.1). Sunlight was the world's first individually-packaged, brand-name laundry soap.

As the world population reaches 7.3 billion, large quantities of laundry bar soaps are widely used in developing countries with low per capita incomes.

Laundry bars are used either alone or in conjunction with powder detergents, depending on local economics, washing customs, and the availability of washing machines.

Figure 9.1 Sunlight Soap.

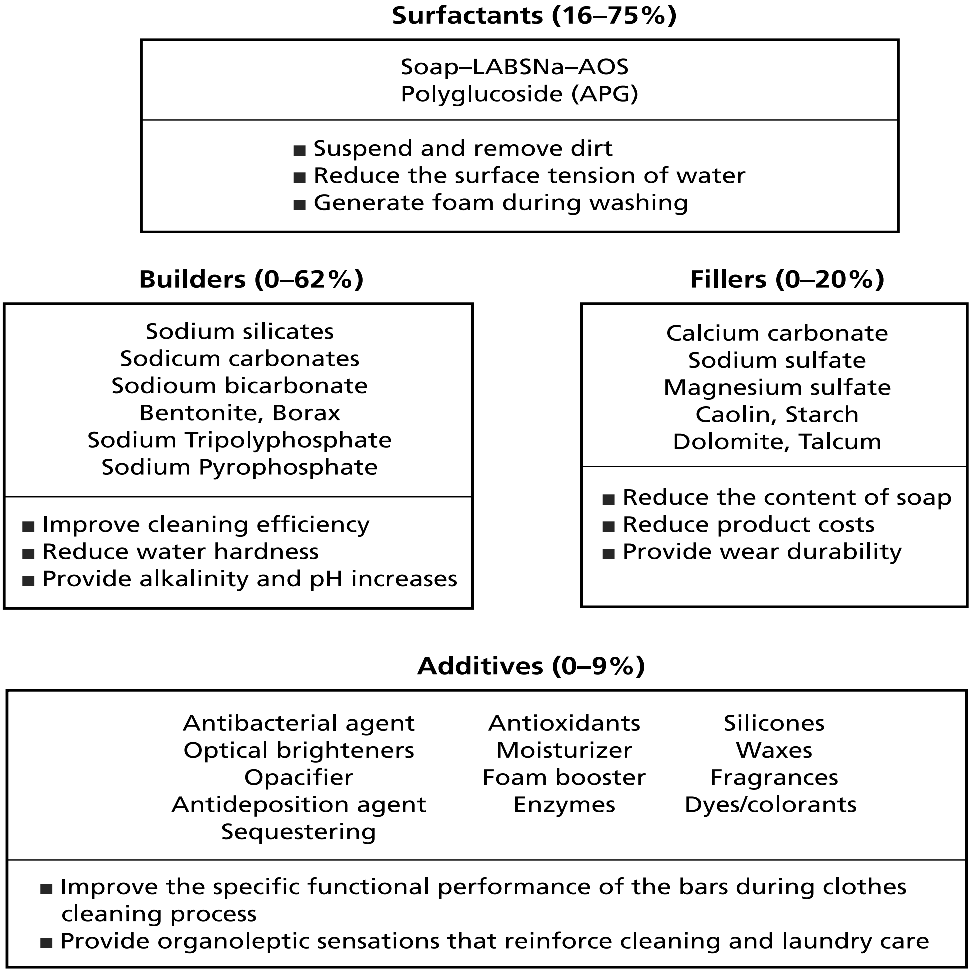
Laundry Bar Types

There are three categories of laundry products in bar form: soap, synthetic (syndet), and a soap/syndet combination (combo) (Berna et al., 1998). Figure 9.2 summarizes composition, ingredients, and performance characteristics of laundry bar soaps. Common formulations of combos and syndets are found in Tables 9.1, 9.2, and 9.3.

Soap Laundry Bars

Soap laundry bars are produced from animal- and vegetable-based fats and oils raw materials. Soap laundry bars are comprised of one of the following formulas:

- Pure laundry soap without builders or fillers
- Filled laundry soap with builders or fillers



Surfactants (16–75%)

Soap–LABSNa–AOS
Polyglucoside (APG)

- Suspend and remove dirt
- Reduce the surface tension of water
- Generate foam during washing

Builders (0–62%)

Sodium silicates
Sodicum carbonates
Sodioum bicarbonate
Bentonite, Borax
Sodium Tripolyphosphate
Sodium Pyrophosphate

- Improve cleaning efficiency
- Reduce water hardness
- Provide alkalinity and pH increases

Fillers (0–20%)

Calcium carbonate
Sodium sulfate
Magnesium sulfate
Caolin, Starch
Dolomite, Talcum

- Reduce the content of soap
- Reduce product costs
- Provide wear durability

Additives (0–9%)

Antibacterial agent	Antioxidants	Silicones
Optical brighteners	Moisturizer	Waxes
Opacifier	Foam booster	Fragrances
Antideposition agent	Enzymes	Dyes/colorants
Sequestering		

- Improve the specific functional performance of the bars during clothes cleaning process
- Provide organoleptic sensations that reinforce cleaning and laundry care

Figure 9.2 Laundry bar composition, ingredients, and performance characteristics.

Table 9.1 Combo Bars Formulation without Enzymes

Components	Range (%)	Typical (%)
Soap (29% of moisture)	60–72	66
Active ingredient—LABSNa	3–10	8
Sodium silicates—Na_2SiO_3 (42%) $Na_2O:SiO_2 = 1:2$	1–5	2
Solids builders and fillers	2–8	4
Fragrances	0.5–1.0	1
Water (H_2O)	18–25	19
Dyes	0.03–0.05	0.03
	Total	100

Table 9.2 Combo Bars Formulation with Enzymes

Components	Range (%)	Typical (%)
Soap (25% of moisture)	63–68	65
Anionic surfactant	3–10	5
Sodium silicate	1–5	3
TPP/sodium carbonate	3–9	7
Fragrances	0.5–1.0	1
Water (H_2O)	10–24	13.3
Enzymes (protease)	0.1–3.0	0.2
Borax (for enzyme protection)	1.5–3.0	2
Glycerol (for enzyme protection)	2–4	2.5
Dyes	0.03.–0.05	0.03
	Total	100

Table 9.3 Syndet Bars Formula

Components	Range (%)	Typical (%)
Active ingredient—LABSNa	16–25	18
Sodium sulfate—NA_2SO_4 (anhydrous)	10–18	13
Sodium carbonate—Na_2CO_3	5–10	10
Calcium carbonate—$CaCO_3$	20–25	20
Caustic soda —NaOH (50%)	0–2	1
Bentonite—Al_2O_3—$4SiO_2$—$4H_2O$	20–25	18
Sodium silicates—Na_2SiO_3 (42%) $Na_2O:SiO_2 = 1:2$	2–5	4
Fragrances	0.1–1.0	0.5
Water (H_2O)	12–18	15.5
Dyes	0.03–0.05	0.03
	Total	100

Soap/Synthetic Laundry Bars (Combo)

Combo laundry bars consist of soap with synthetic formulation combined with solid and/or liquid builders and fillers.

Synthetic Laundry Bars (Syndet)

Syndet laundry bars are made from synthetic raw materials derived from petroleum chemical components and some vegetable source materials. Synthetic soap is produced with finishing line machinery.

Laundry Soap Vacuum Spray Drying

The vacuum spray drying plant reduces the moisture content of the liquid neat soap, converting it into dry soap (Figures 9.3). The spray chamber can connect with four types of plodders. The choice depends on the type of finished laundry bar formulation required.

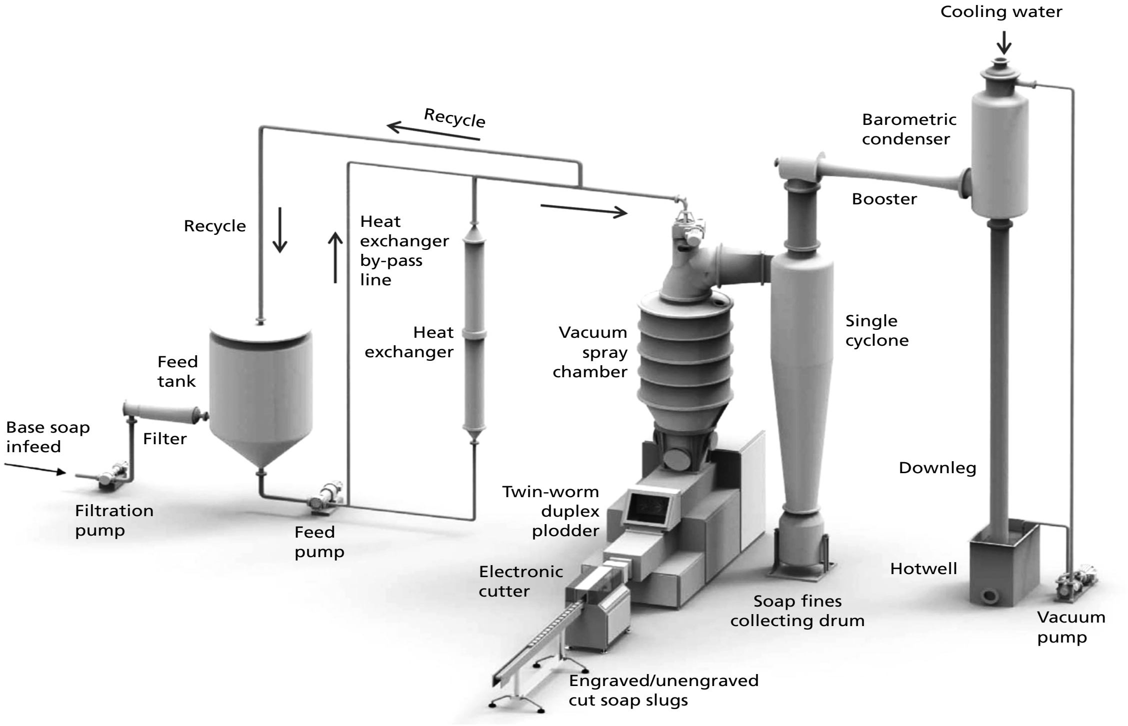


Figure 9.3 Laundry bar soap vacuum spray drying plant.
Source: Soaptec Srl.

Vacuum spray drying systems are easy to operate and are flexible for the production of various formulations (with and without builders or fillers) at different moisture levels. The processing steps for laundry bar soap production with vacuum spray drying plants are:

1. Mixing all solids, liquids, and additives with neat soap in a crutcher
2. Formulating soap feeding with a positive displacement pump
3. Pre-heating in a vertical shell-and-tube heat exchanger (only for higher than 68% TFM soaps)
4. Liquid filler injection (if applicable)
5. Spraying the heated neat soap into the spray chamber under vacuum to obtain dry soap
6. Extruding finished laundry bars or laundry soap base in pellets
7. Adding perfume and color by dosing systems into the final plodder (Since the soap is already dried and cooled, perfume loss will be minimal.)
8. Cutting the extruded soap into individual length slugs
9. Engraving the slugs or stamping into bars
10. Packaging individual or multiple engraved or stamped bars

Crutcher Applications

The crutcher is an efficient, versatile mixer used to add solid and liquid builders, fillers, and minor additives to the base soap before the spray drying step (Figure 9.4).

The crutcher is a jacketed vessel with a vertical screw-type agitator inside a draft tube. The rotating screw produces a vigorous vertical flow of the material across the vessel (down and up), resulting in very good mixing. Crutcher applications for less than 5% and more than 5% solids additions are shown in Figures 9.5 and 9.6.

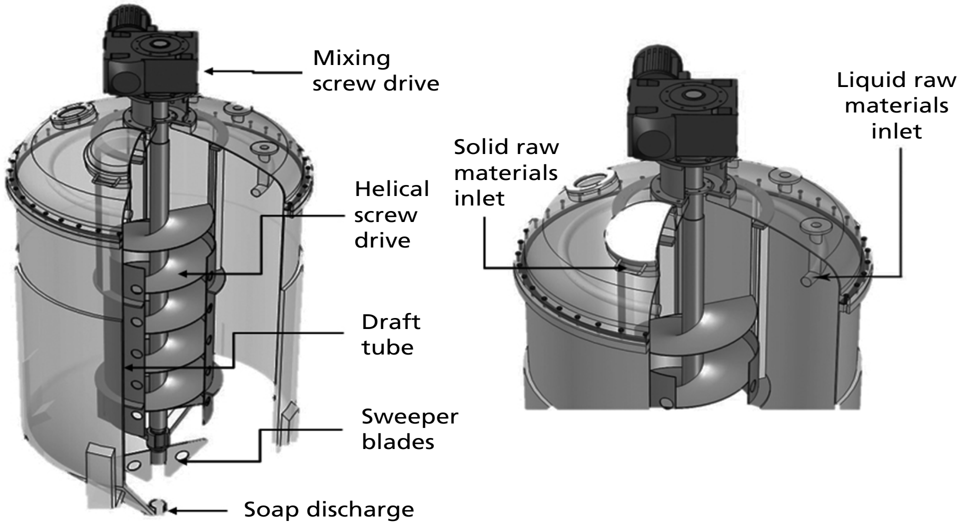


Figure 9.4 Illustration of a crutcher.

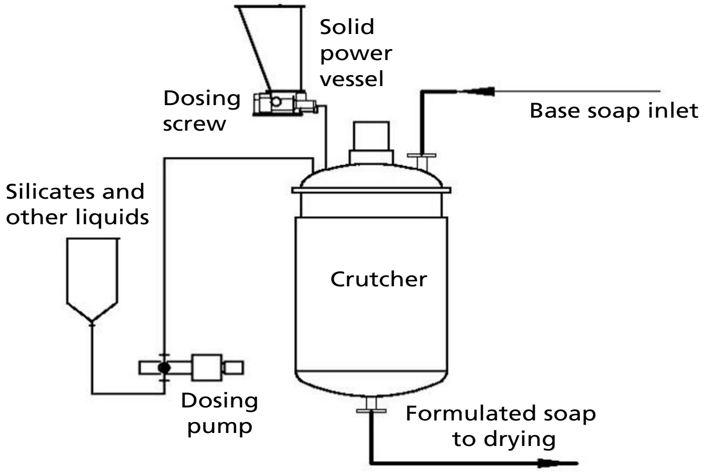


Figure 9.5 Typical system for addition of solid and liquid ingredients for laundry bars (with less than 5% solids addition).
Source: Binacchi & Co.

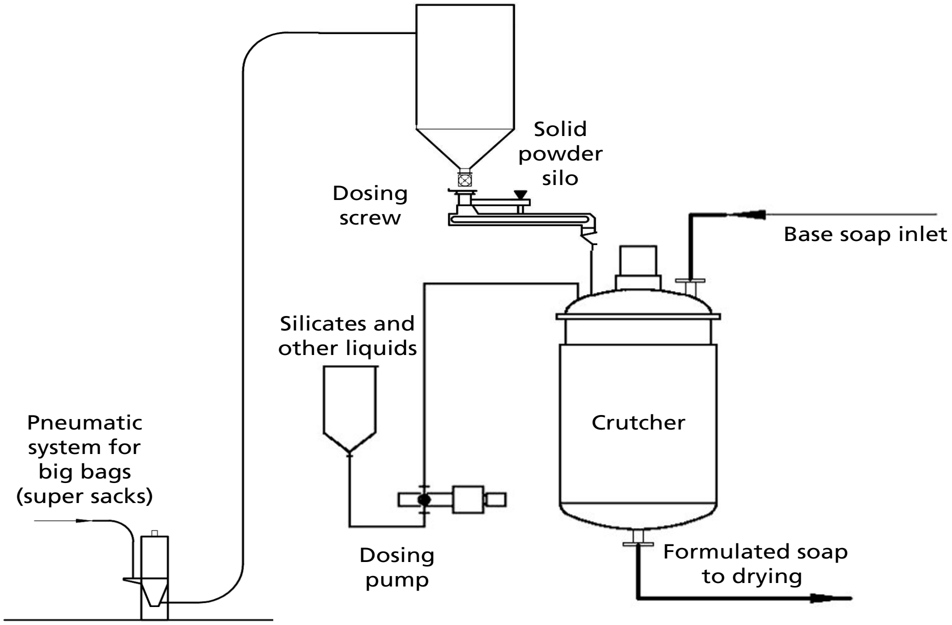


Figure 9.6 Typical system for addition of solid and liquid ingredients for laundry bars (with more than 5% solids addition).
Source: Binacchi & Co.

Laundry Bar Soaps Processing Plant

A vacuum spray drying plant for the production of filled opaque, pure opaque, and/or translucent laundry bar soaps is shown in Figure 9.7. Two additives systems are shown:

1. sodium silicate solution tank and dosing pump to by-pass the heat exchanger
2. a dosing pump synchronized with the soap feed pump thay proportions perfumes and color solution into the duplex plodder

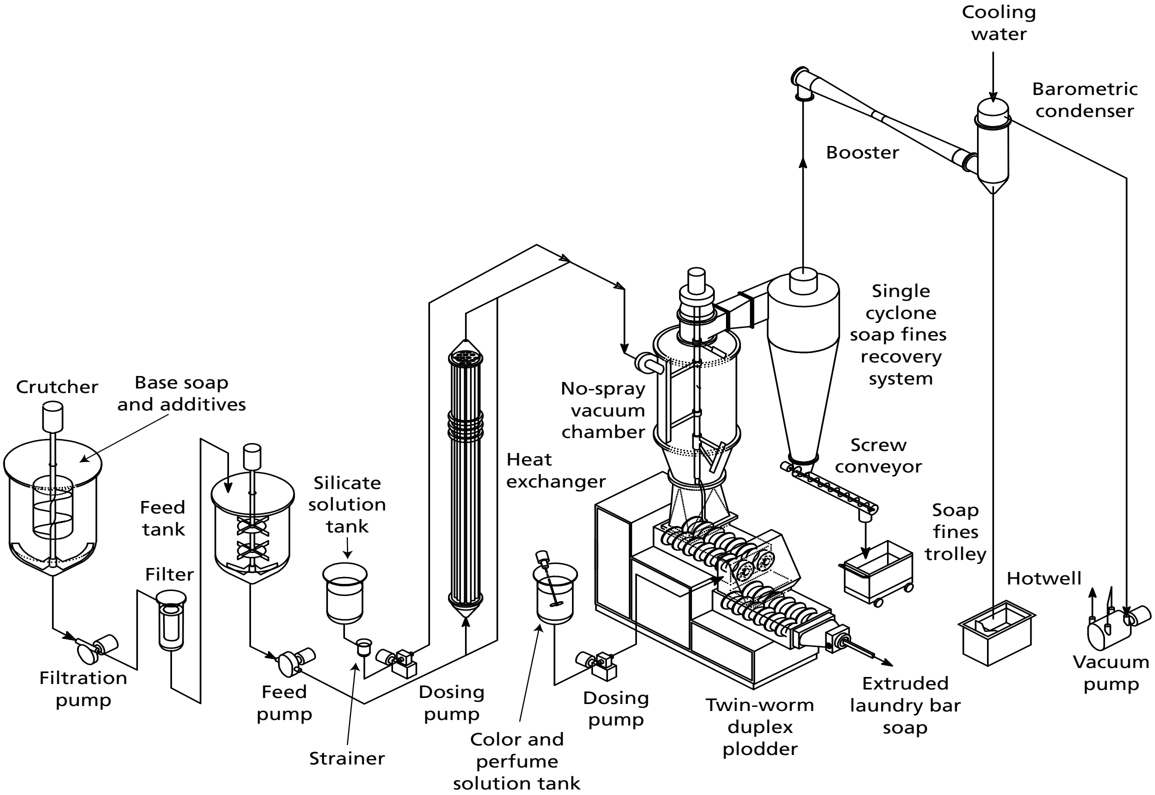


Figure 9.7 Laundry bar soap vacuum spray drying plant with additive systems.
Source: Mazzoni LB, SpA

Filled Opaque Soaps

Base soap with minor additives mixed and homogenized in the crutcher is filtered and sent to a feed tank and pumped through the heat exchanger in the no-spray vacuum chamber. The vapors created by flashing under vacuum are condensed in a barometric condenser. Soap fines generated upon flashing are carried over the vapors and are recovered in a single cyclone separator with a fines extruder screw conveyor, which feeds the fines into a collector trolley to the drum.

A duplex plodder extrudes the laundry soaps. Besides the most commonly used duplex plodder, triplex plodders are also used for higher quantity and more additives and

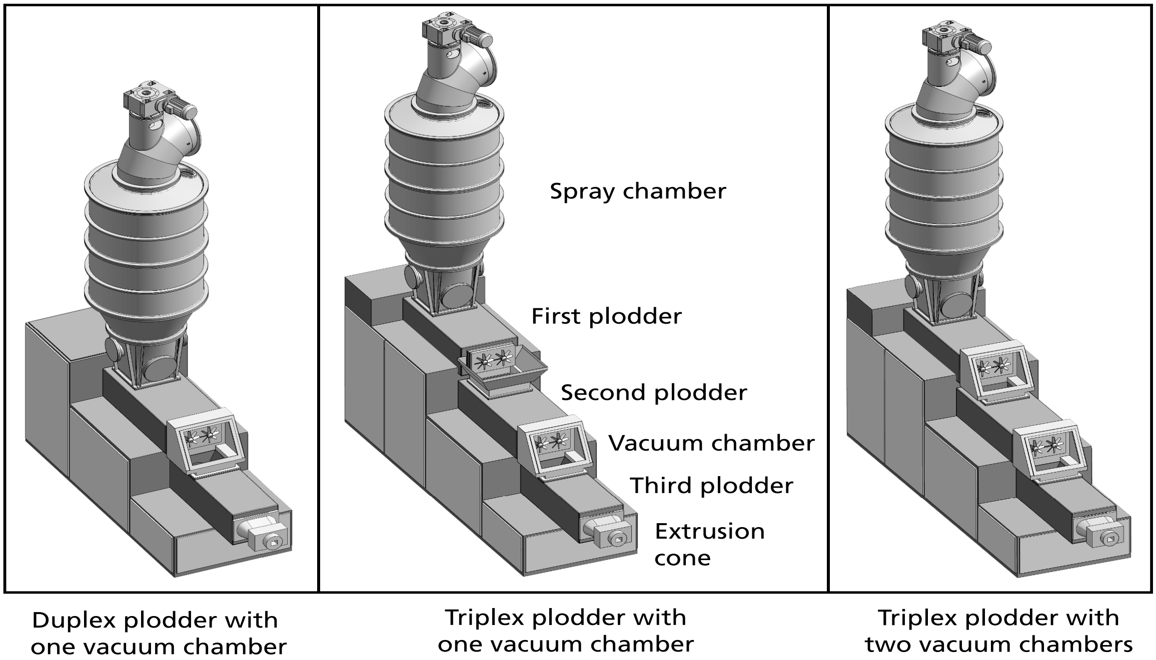


Figure 9.8 Plodder types used with the vacuum spray chambers for soap dryers.

translucent soaps, which require more mechanical working of the soap (Figure 9.8). A cutter cuts the continuous slugs into individual-length slugs. Optional engraving rollers are mounted on the cutter.

Pure Opaque Soaps

Base soap from the saponification plant is fed directly into the feed tank and pumped through a heat exchanger for low water content soaps, or it is by-passed for high water content bars. The soap enters the "no-spray" vacuum chamber and is subject to the same process as for filled opaque.

Translucent Soaps

Base soap from the saponification plant is mixed with proper amounts of glycerine, PEG, and sorbitol in the crutcher and then it goes into the feed tank. From the feed tank, soap is pumped through a heat exchanger and is then sent to the no-spray vacuum chamber, and is subject to the same processing as the other soaps.

Extrusion Slugs Shaping and Engraving

Extrusion Die Plates

From the extrusion cone of the last plodder, the product is extruded in shaping die plates (orifices) fitted at the end of the cone. Figure 9.9 illustrates single and extension dual extrusion die plates.

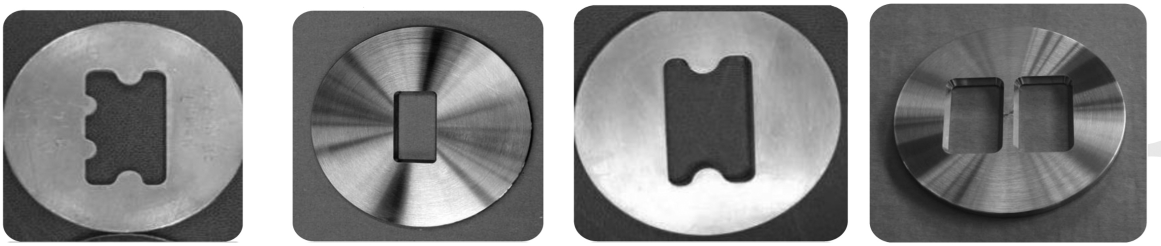


Figure 9.9 Slug shaping extrusion die plates (orifices) fitted to plodders.

Unengraved and Engraved Slugs

The extruded slugs can be left unengraved or can be engraved (Figure 9.10) with an engraver roll fitted on electronic cutters.

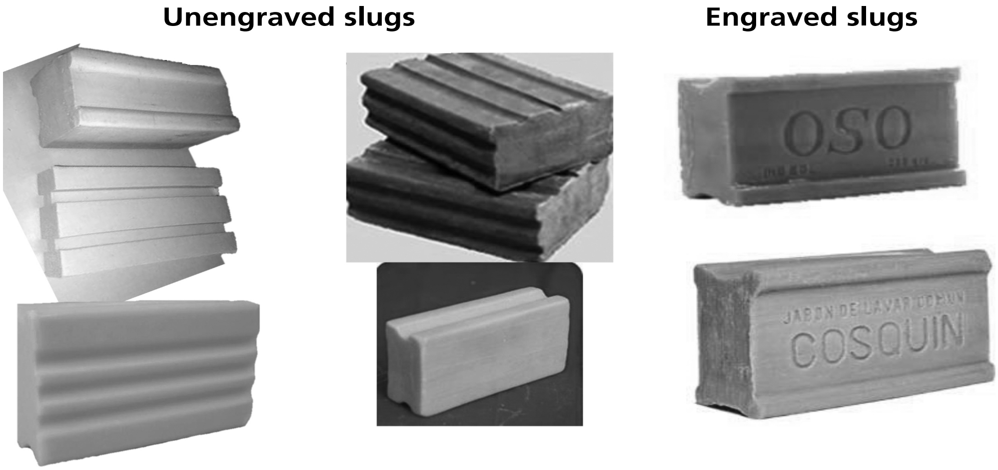


Figure 9.10 Unengraved and engraved extruded slug shapes.

Cutter with Engraver Rolls

The Binacchi electronic cutter with three blades cuts the extruded slugs into individual-length slugs. Engraving rolls mounted on the in-feed engrave and center designs and logos on both sides of the slug.

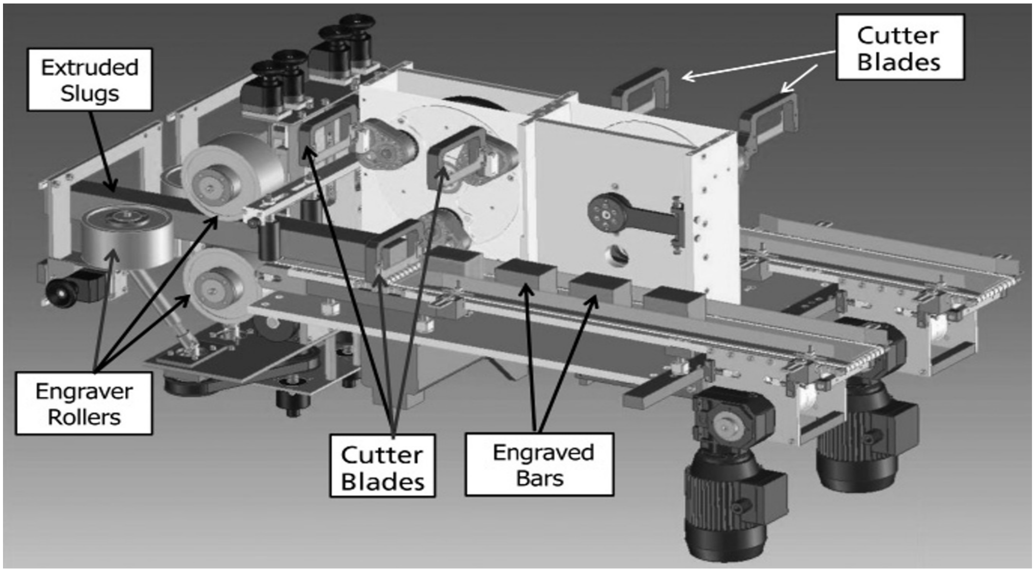


Figure 9.11 Binacchi three-blade electronic cutter with engraver rolls.
Source: Binacchi & Co.

Efflorescence

Efflorescence, also referred to as *whiskers,* is fine, white, hair-like deposits that appear on the surface of the soap bars. They are white sodium oleate crystals of pure soap or a mixture of oleate:laurate (see Figure 9.12).

Efflorescence Formation Mechanism

The alkali in silicate absorbs carbon dioxide (CO_2) from the air during mixing with soap, forming sodium carbonate hydrate:

$$Na_2O \cdot SiO_2 + CO_2 \rightarrow Na_2CO_3 + SiO_2$$

The volume of the hydrated sodium carbonate is much higher than the original alkali silicate. As hydrated sodium carbonate is forming in the soap, it forces apart and weakens the structure of the soap.

Efflorescence is formed because water containing soap oleate, and a mixture of oleate and soluble laurate evaporates from the surface of the soap. CO_2 is less soluble in alkaline solutions and requires more time to form Na_2CO_3.

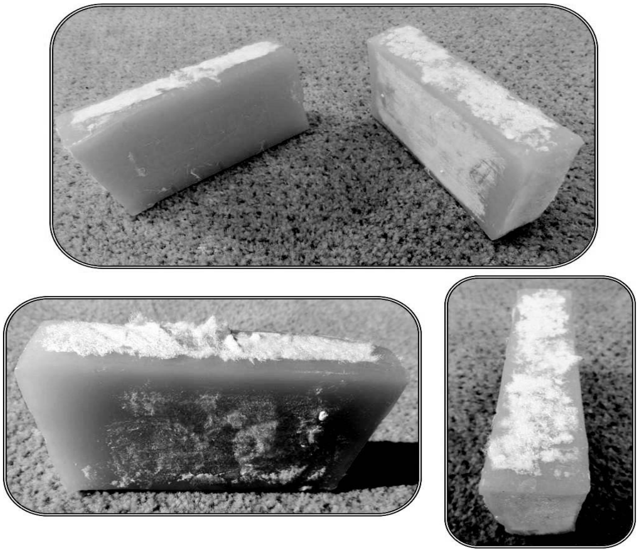


Figure 9.12 Efflorescence

Since most soap water loss has already occurred and the bar surface is dry, the oleate will deposit below the surface without forming efflorescence. To minimize or practically eliminate efflorescence:

1. Always use alkaline silicate 2:1 $SiO_2 : Na_2O$ (5% minimum). Neutral 3:1 ratio types should not be used.
2. Preheat the silicate near the soap temperature before adding to the mix.
3. Ensure that the mixture is fully homogeneous.
4. Do not add water to the soap–silicate mixture—especially cold water. If water addition is unavoidable, the temperature should be similar to the temperature of the mixture.
5. Store the finished product in an 80% relative humidity (RH) area. In low RH, the drying rate of the soap surface is high and efflorescence stops. Even for low moisture content soaps there is no supply of sodium oleate to the surface, thus no efflorescence.

Combo Laundry Bar Production

All ingredients required for a combo bar are fed into a crutcher for full reaction, mixing and homogenizing with the soap, which is also fed into the crutcher. Drying the formulated mixture and extrusion in form bar are done with vacuum spray dryers (Figure 9.13, p. 214).

Syndet Laundry Bar Production System

The production system for syndet laundry bars consists of a liquid and solid materials storing and dosing section (Figure 9.14, p. 215). All the materials are fed into a double-arm sigma mixer, which is the first of three optional lines illustrated in Figures 9.15, 16, and 17 (p. 216). (For details about all the machinery used in these lines refer to Chapter 8, Bar Soap Finishing.) Syndet laundry bar formulations are shown in Table 9.4 (p. 218).

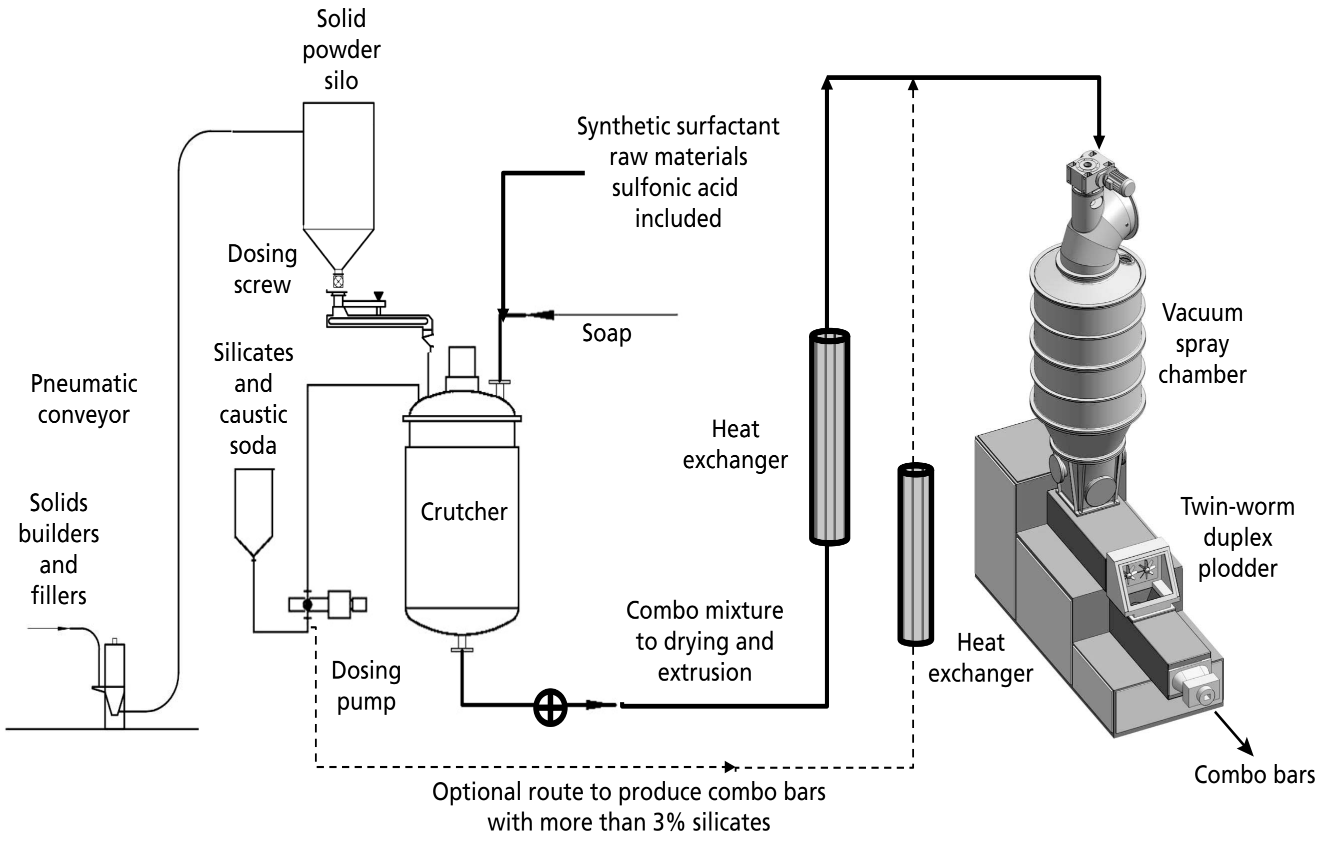


Figure 9.13 Combo laundry bars production system.

Notes: Synthetic surfactant: 5% min.; sulfonic acid: 5% max; solids builders and fillers: 5% min.; silicates: 5% max

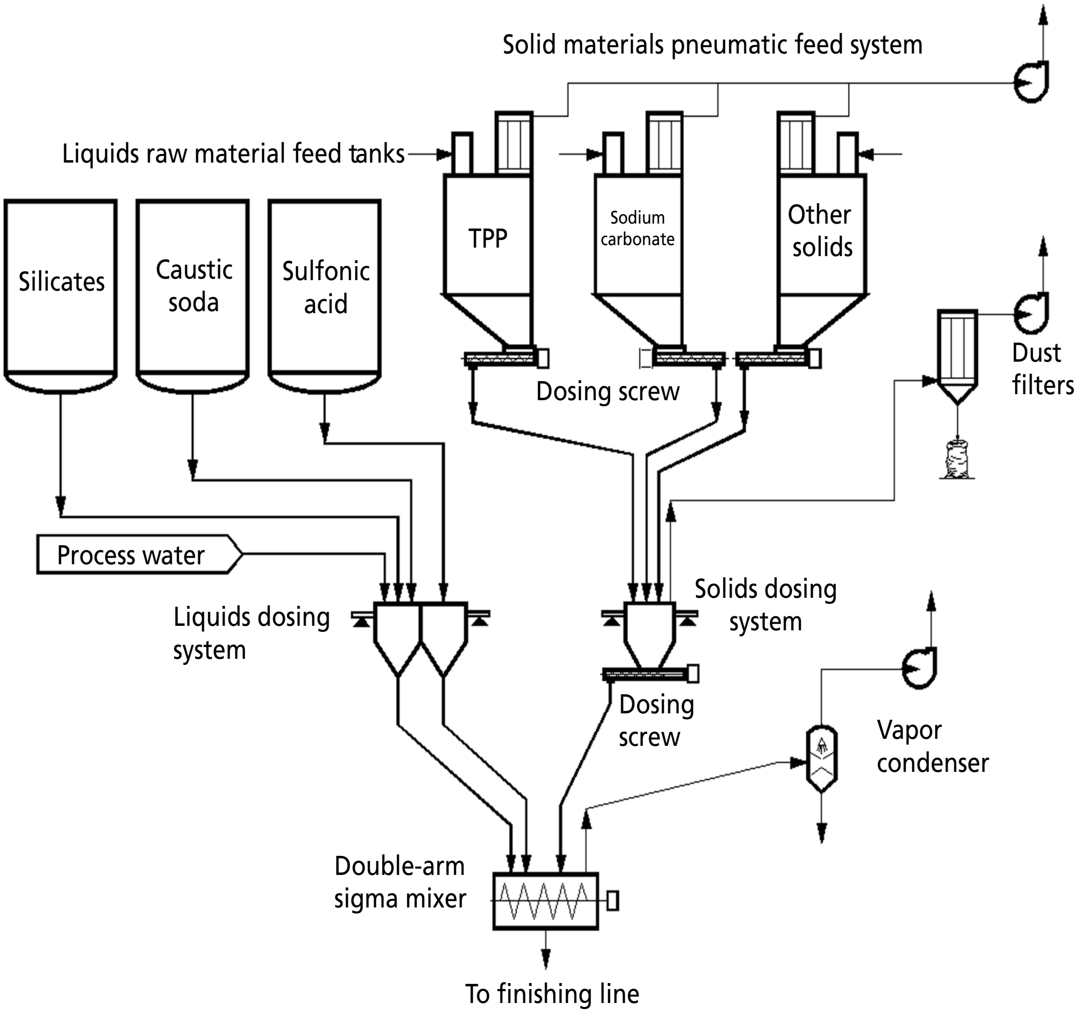


Figure 9.14 Typical production line for syndet laundry bars.

Source: Desmet Ballestra SpA.

Syndet Laundry Bar Finishing Lines

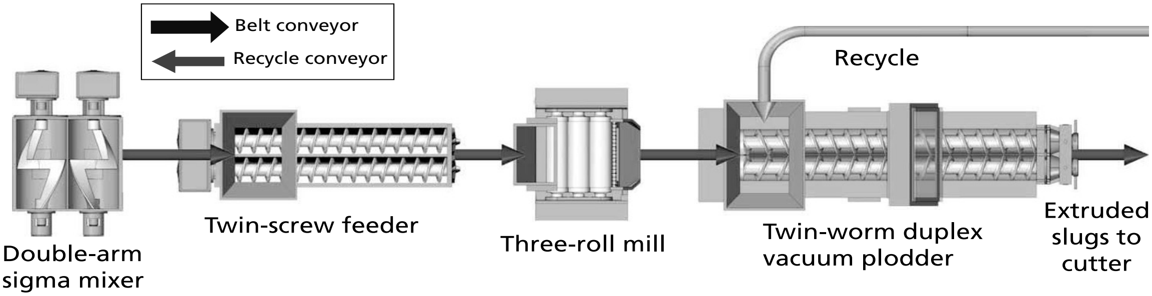


Figure 9.15 Syndet laundry bar soap finishing line, type 1.

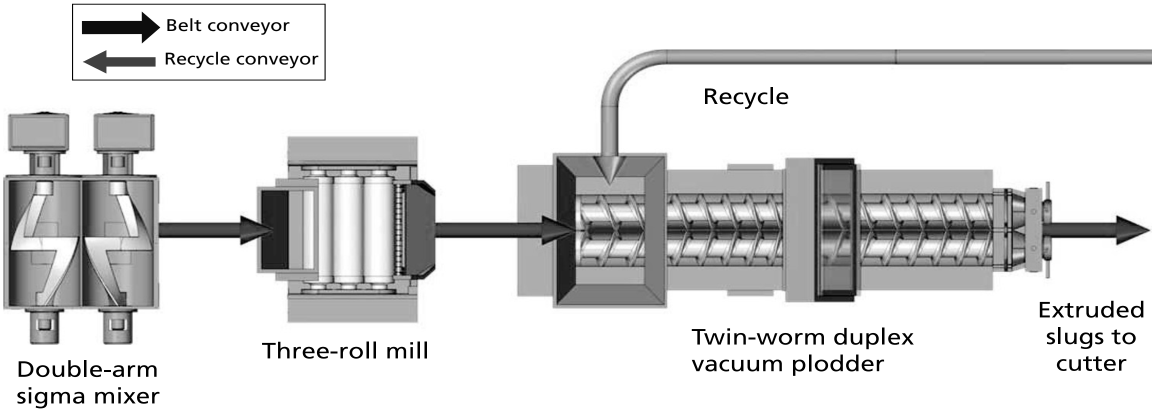


Figure 9.16 Syndet laundry bar soap finishing line, type 2.

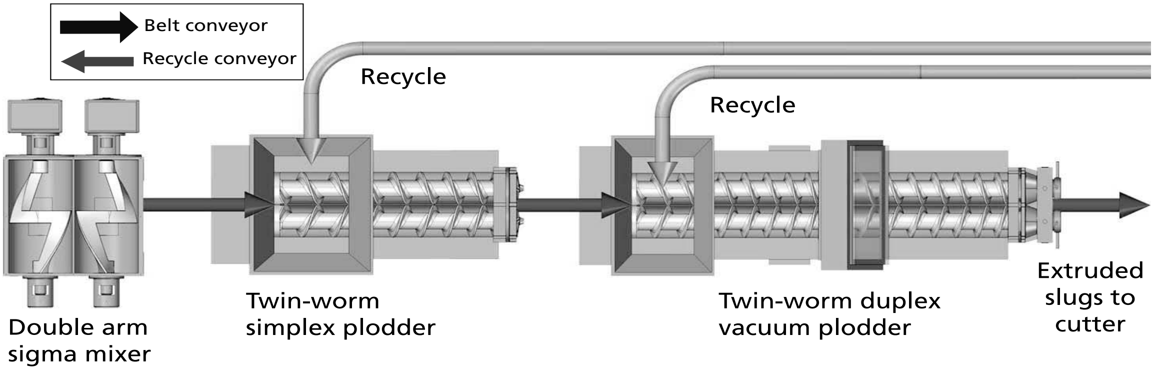


Figure 9.17 Syndet laundry bar soap finishing line, type 3.

Table 9.4 Standards for Laundry Bars in Several Countries

Country	Classification	Specification
Colombia NTC 527	Type 1	TFM: 32.5–48.0 Anhydrous soap: 35–52%
	Type 2	TFM: 48% min. Anhydrous soap: 52% min. Alkalinity as NaOH: 0.20% max. Sodium silicate: 16% max. Builders (Phosfates, carbonates): 20% max
Costa Rica	Type B	TFM: 65% min.
	Type C	TFM: 30% min.
Mexico NMX-Q-1982	Normal	Anhydrous soap: 60–70% min. Water contents: 35% max. Free alkalinity as NaOH: 0.05% max. Chlorides as NaCl: 1.0 max. Silicate: 13% max.
Venezuela (1) Convenio 1540-99	Soap solid bars	TFM: 48% min. Alkalinity as NaOH: 0.3% max. Synthetic surfactant: < 3.0% Builders and additives: 20% max. Water and volatiles: 36% max.
	Soap flakes	TFM: 60% min. Alkalinity as NaOH: 0.5% max. Synthetic surfactant: < 3.0% Builders and additives: 10% max. Water and volatiles: 20% max.
	Soap powder	TFM: 30% min. Alkalinity as NaOH: 2.5% max. Synthetic surfactant: < 3.0% Builders and additives: 10% max. Water and volatiles: 30% max.
	Soap in past or liquid	TFM: 25% min. Alkalinity as NaOH: 0.3% max. Synthetic surfactant: < 3.0% Builders and additives: 20% max. Water and volatiles: 70% max.
	Combo solid bars	TFM: 30% min. Alkalinity as NaOH: 0.3% max. Synthetic surfactant: < 3.0% Builders and additives: 20% max. Water and volatiles: 36% max.
	Combo powder	TFM: 20% min. Alkalinity as NaOH: 2.5% max. Synthetic surfactant: < 3.0% Builders and additives: 10% max. Water and volatiles: 70% max.

Continued

Table 9.4 Continued

Country	Classification	Specification
	Combo paste or liquid	TFM: 15% min. Alkalinity as NaOH: 2.5% max. Synthetic surfactant: < 3.0% Builders and additives: 20% max. Water and volatiles: 70% max.
India (BIS)	Grade I	TFM: 76% min.
	Grade II	TFM: 70% min.
	Grade III	TFM: 60% min.
	Bathing bar	TFM: 40% min. + 4% surfactant

Laundry Bar Types

Figure 9.18 Combo, syndet, two-color, and mottled laundry soaps.

Laundry Bar Shapes

Balls and cylinders

Rectangular

Figure 9.19 Bar shape types—single and multi-packs.

Reference

Berna, J.L.; Moreno, A.; and Bengoechea, C. Laundry Products in Bar Form, *Journal of Surfactants and Detergents,* AOCS Press, Vol. 1., No. 2, April 1998.

Acknowledgement

The assistance of Binnachi & Co., Desmet Ballestra SpA, Soaptec srl, and Mazzoni LB, all of which provided material for this chapter, is very much appreciated.

10 Multicolored and Multicomponent Soap Manufacturing Systems

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Introduction

Multicolored/multicomponent soaps offer potential marketing advantages over single-color soaps with or without additives. The visual differentiation over single-color soaps provides aesthetic advantages for the multicolored types, and for the multicomponent soap, differentiation can show the ingredient(s) which claim to enhance product performance.

Multicolored and Multicomponent Soap Types

There are four distinct types of multicolored and multicomponent soaps available: marbleized, striped, speckled, and two-tone.

In the soap type and manufacturing method descriptions, the *primary base* refers to the larger quantity, predominant color soap base. The *secondary base* is the lesser quantity second color base.

Marbleized

Marbleized (also called marbled, variegated, and mottled) soaps are produced by dosing or injecting an additional color into the primary base soap, which can be white or colored.

Striped

Striped soaps with well-defined linear designs are produced by the controlled addition (injection) of a secondary base of one color into a primary base of another color.

Speckled

Speckled soaps are formed by the proportioned addition of small speckles (granules) or larger chunks of different colors and/or types of product added into the primary base.

Speckled soap with granules

Speckled soap with chunks

Two-Tone

Two-tone toilet and laundry soaps are formed when the primary and secondary bases are fed into nontangential twin-worm plodders. These plodders are side-by-side with separate worm barrels and individual worms. The two different bases move through the plodder separately until extrusion. Side-by-side, vertical, horizontal, diagonal, radial, and multiple patterns can be produced.

Handcrafted Artisan Soaps—An Old/New Niche Market

The handcrafted (also known as handmade or homemade) soaps with special ingredients, performance claims, and very interesting designs, have grown worldwide. What started as a hobby for many home soapmakers grew into small-business enterprises. In 1998, the Handcrafted Soap Makers Guild (HSMG) was formed with these objectives: "to promote the handcrafted soap industry, to act as a center of communications among soap makers, and to circulate beneficial information to them." In 2013, the Guild became The Handcrafted Soap and Cosmetics Guild (HSCG). The current worldwide membership is 3,000, and conferences are held yearly. More details are available on the Guild's website: www.soapguild.com.

Manufacturing Systems, Methods, and Product Types

In the soap type and manufacturing method descriptions, the primary base refers to the larger quantity, predominant color soap base. The secondary base is the lesser quantity second color base.

Table 10.1 The Manufacturing Methods presented are based on Mazzoni LB technology.

Manufacturing System	Manufacturing Methods	Product Types
Solid–liquid	■ Color dosing into the extrusion stage plodder ■ Color injection into the extrusion stage plodder ■ Color injection into the extrusion stage plodder barrel	Marbleized
Solid–solid	■ Using two separate single-worm plodders for feeding two different-size soap pellets	Marbleized
	■ Using non-tangential twin-worm plodder	Two-tone
	■ Using speckles, granules and "chunks" feeder group	Speckled
Solid–solid co-extrusion	■ Co-extruder with striping group	Striped
	■ Co-extruder with striping and marbleizing group	Striped and marbleized
Solid–solid–liquid	■ Combination solid–solid and solid–liquid	Striped and marbleized/two-tone striped

Solid–Liquid Systems for Marbleized Soaps

Solid-liquid systems for marbleized soap production consist of a duplex vacuum plodder with a color dosing/injecting group, or a duplex vacuum plodder with a color-dosing group, and a marbleizing group.

Color Dosing into the Extrusion-Stage Plodder

The simplest and most economical method is dosing a color solution into the extrusion stage of the duplex vacuum plodder. The random color distribution (the marbleized effect) is difficult to control (Figure 10.1).

Color Injection into the Extrusion-Stage Plodder Barrel

Another method for color insertion is injecting a color solution into the duplex vacuum plodder's extrusion stage plodder barrel (Figure 10.2).

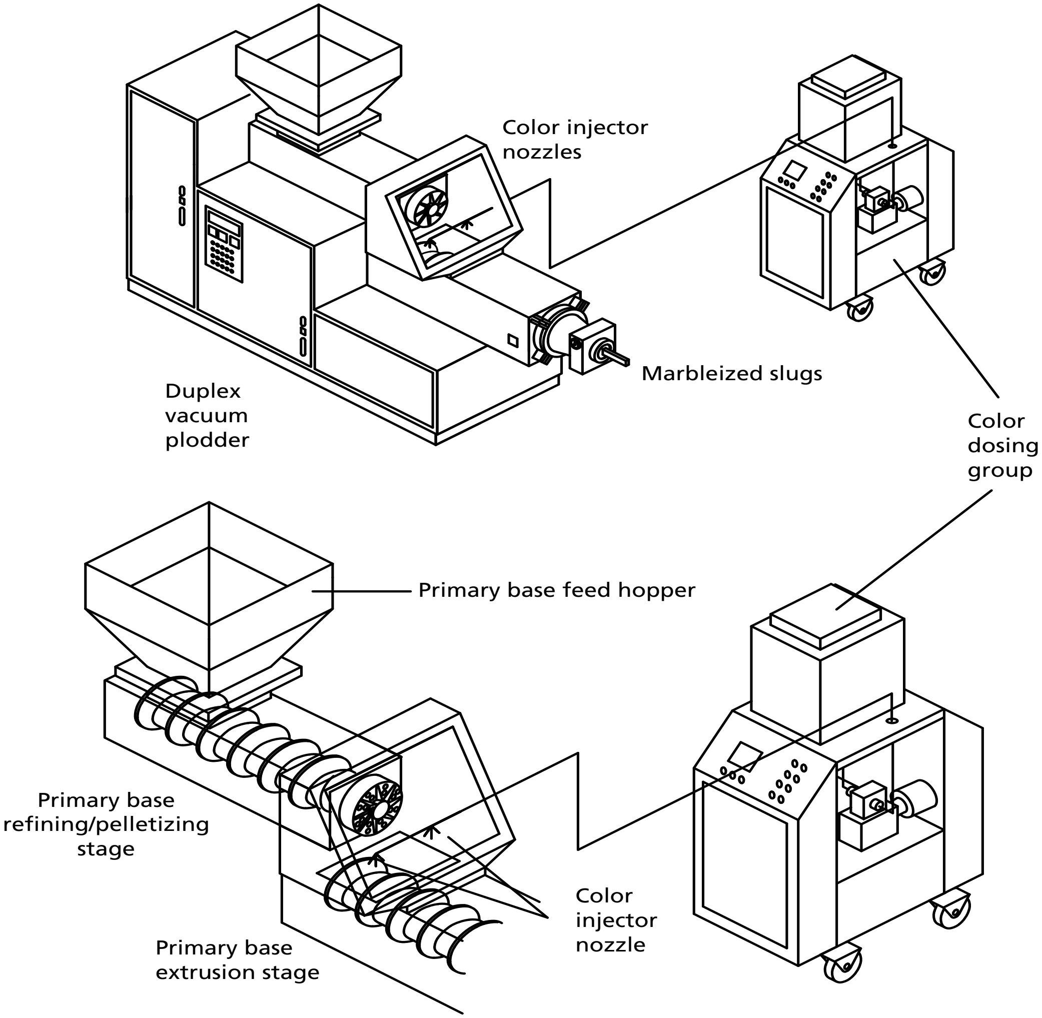


Figure 10.1 Solid-liquid system for marbleized soaps—color dosing into the extrusion stage plodder.

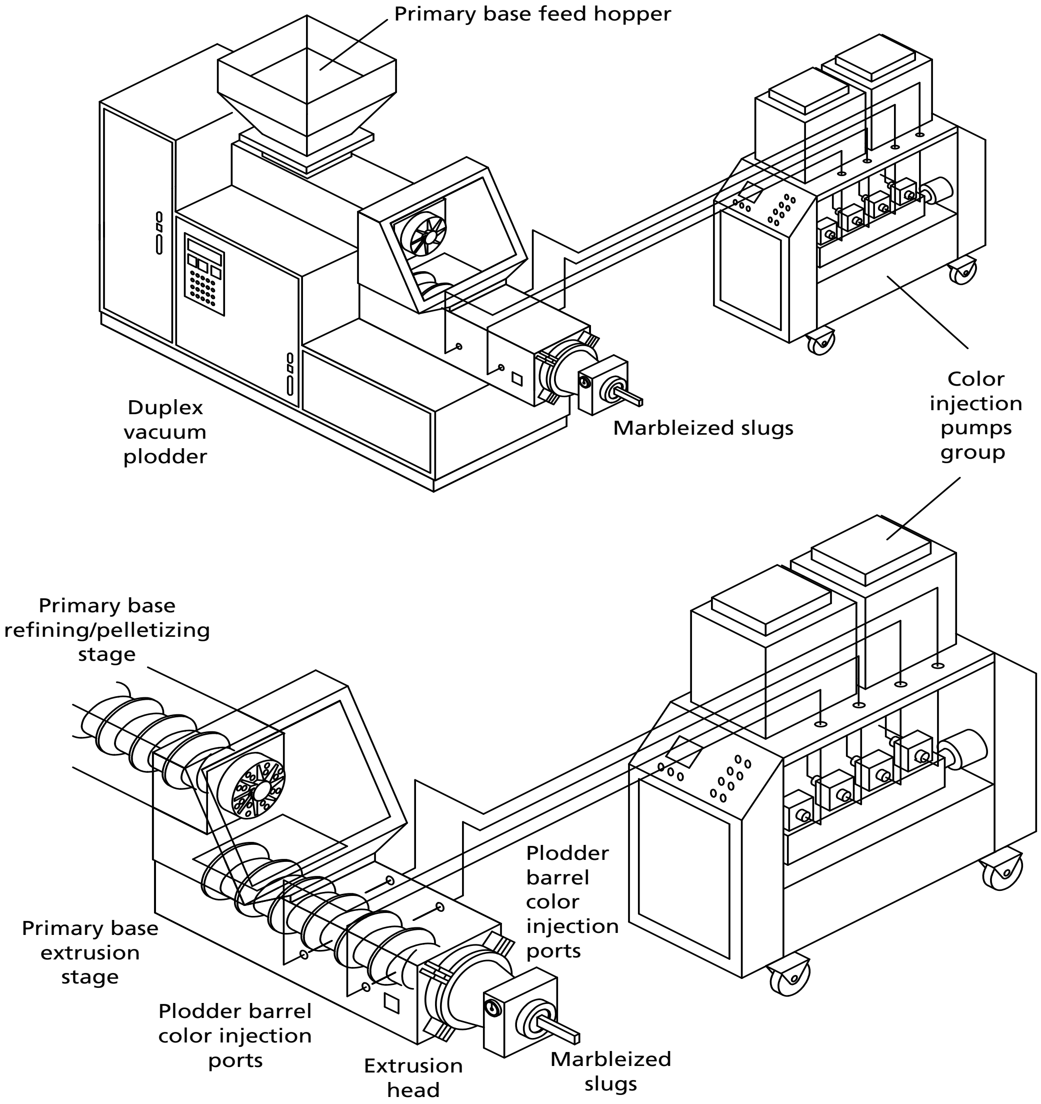


Figure 10.2 Solid–liquid system for marbleized soap—color injection into the extrusion stage plodder barrel.

Color Injection into the Extrusion-Stage Plodder

The color solution is injected through a drilled plate with injection nozzles in the extrusion stage of the duplex vacuum plodder (Figure 10.3). A rotor drive group can be added for independent speed variation of the rotor, allowing one to obtain more marbleizing effects (Figure 10.4). The striping and marbleizing group assembly is shown in Figure 10.5.

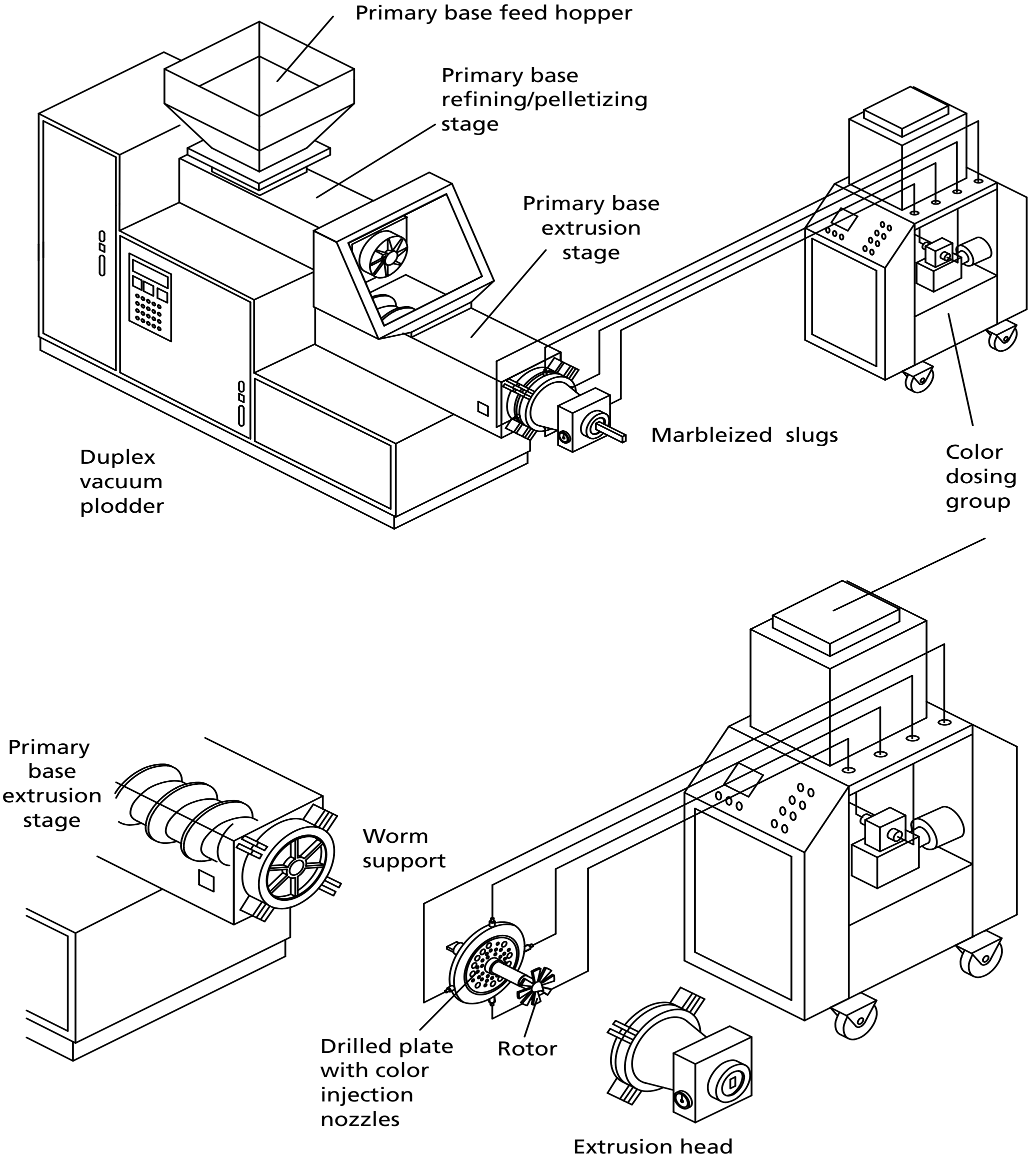


Figure 10.3 Solid–liquid system for marbleized soaps—color injection into the extrusion stage plodder.

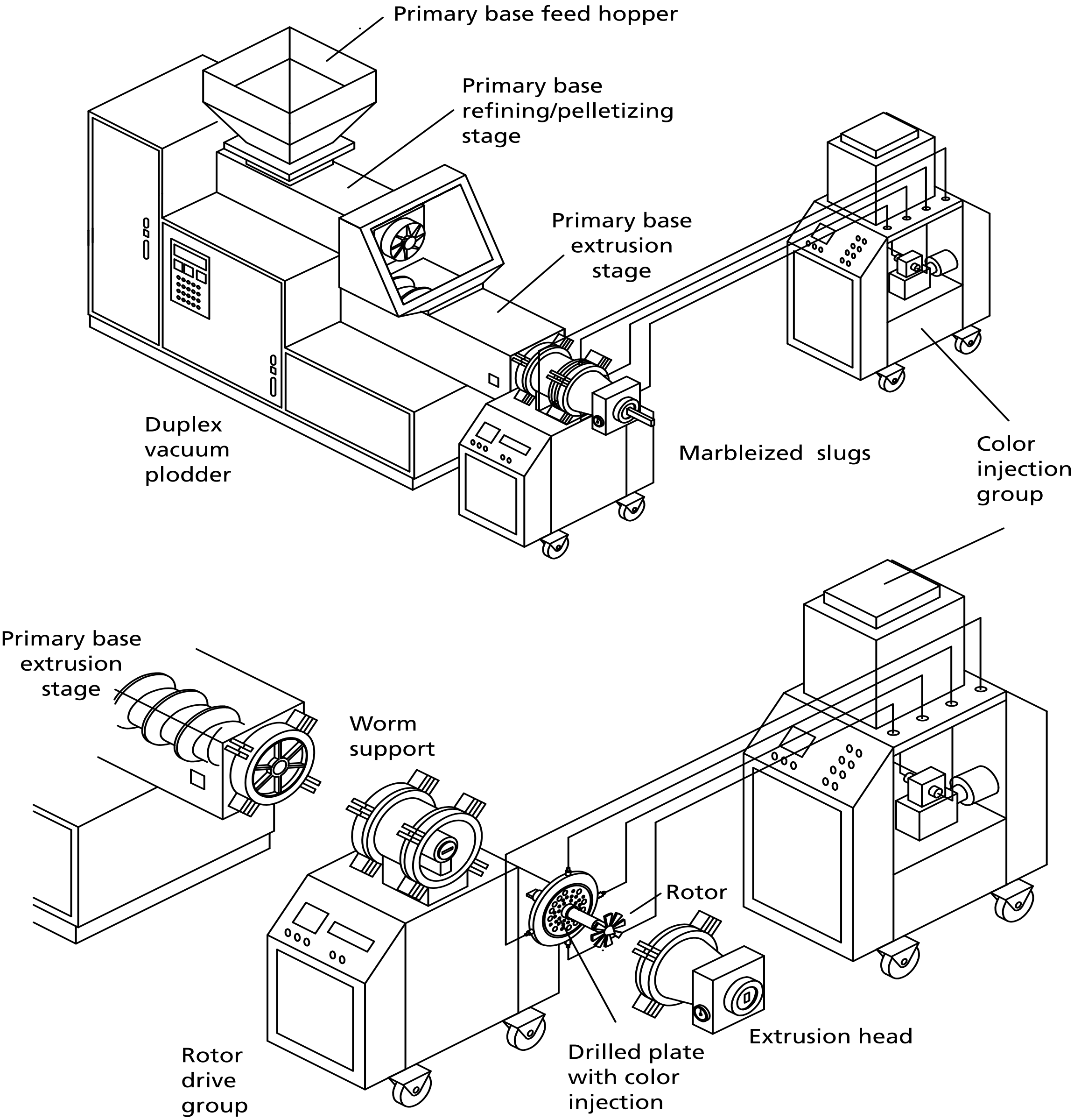


Figure 10.4 Solid–liquid system for marbleized soaps—color injection into the extrusion stage plodder with rotor drive group.

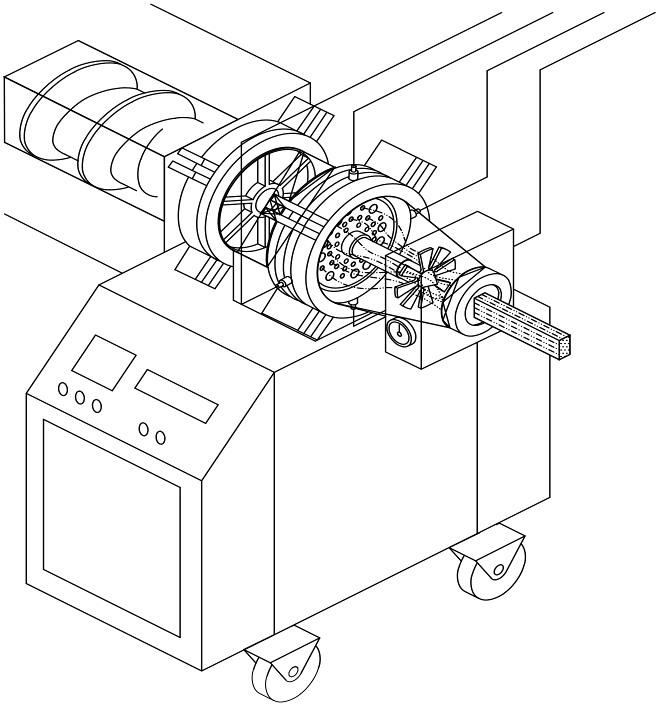


Figure 10.5 Solid–liquid system marbleizing and striping group assembly.

Solid–Solid System for Marbleized Soaps

Utilizing Two Separate Single-Worm Plodders

Two separate single-worm plodders are used to feed two different diameters and lengths of pellets in a predetermined weight ratio into the extrusion stage of a single-worm plodder. The random or partially controlled mixing of the two pellets produces the marbleized effects (Figure 10.6).

Solid–Solid System for Two-Tone Soaps

Utilizing Non-tangential Twin-Worm Plodders

This system utilizes a nonTangential Twin-Worm Duplex Vacuum Plodder. Two different soap bases are fed into each first stage plodder and proceed separately until extrusion. The two bases meet when they reach the extrusion head, which is provided with a baffle. This system can produce various two-tone designs (Figure 10.7, p. 230).

Solid–Solid System for Speckled Soaps

Additives Proportioned into the First-Stage or Extrusion Stage Plodder

Randomly distributed speckles, granules, and small colored soap "chunks" can be added with a feeder group into either the first stage or the extrusion stage plodder (Figures 10.8 and 10.9, pp. 231–232).

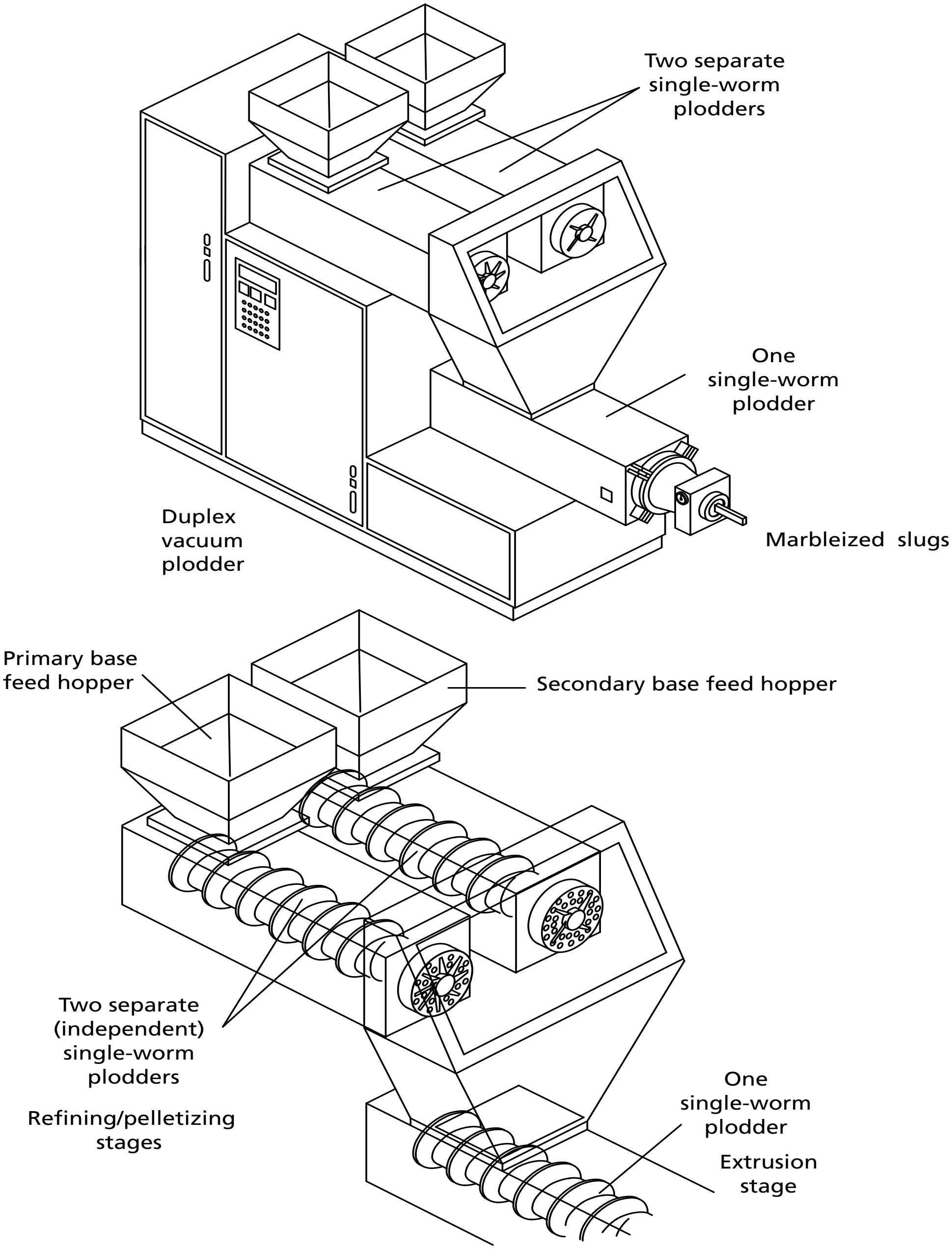


Figure 10.6 Solid–solid system for marbleized bars—utilizing two separate single-worm first stage plodders and one single-worm extrusion stage plodder.

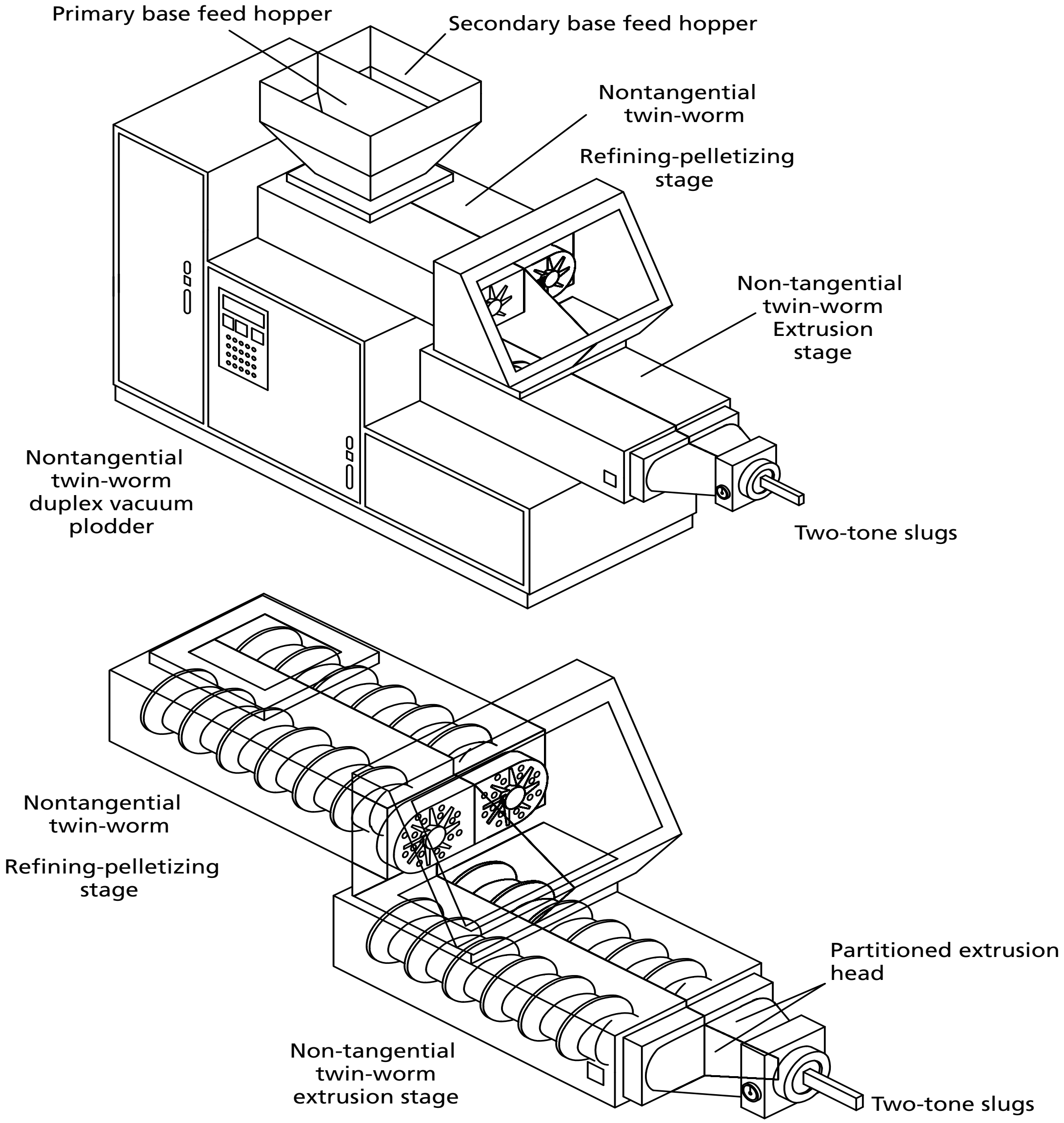
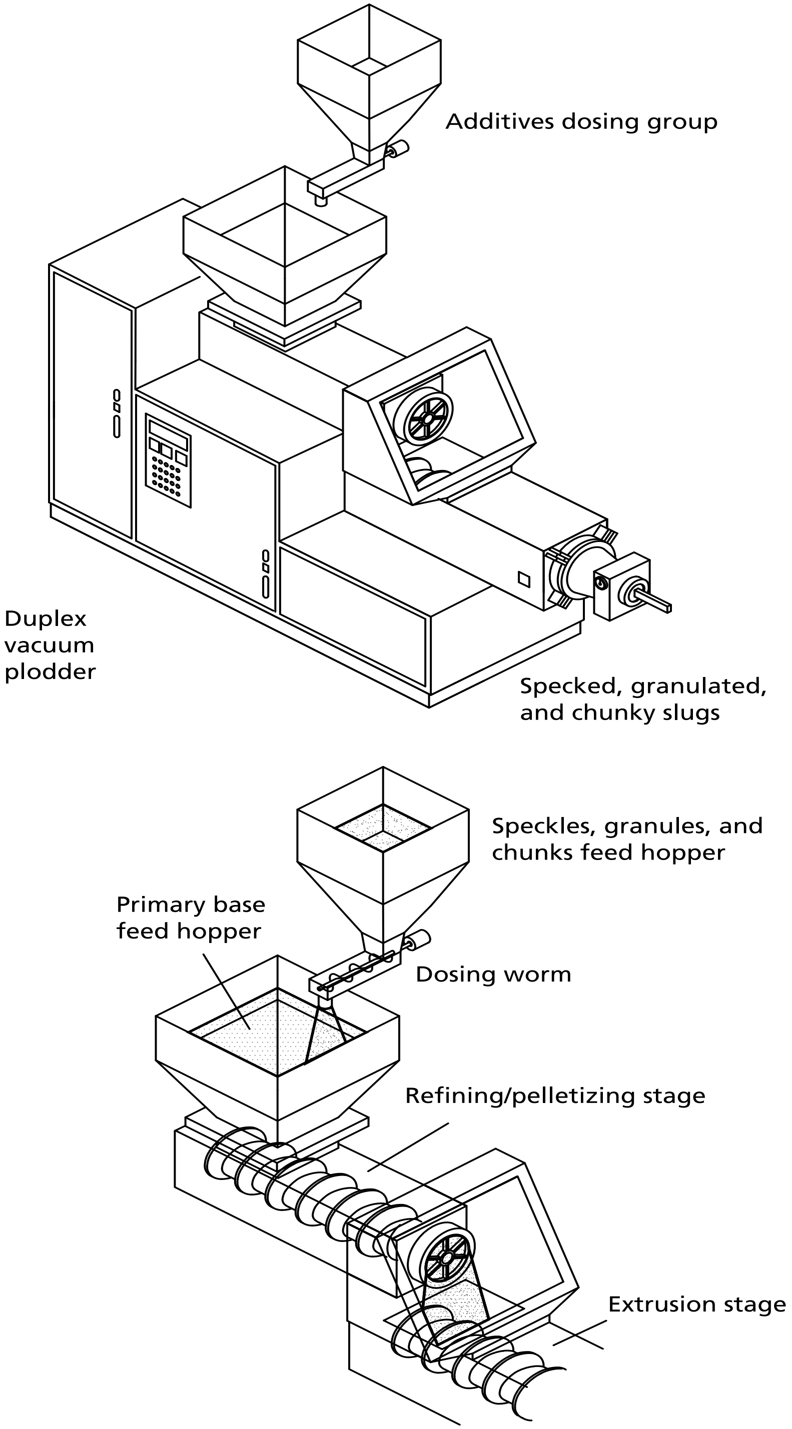
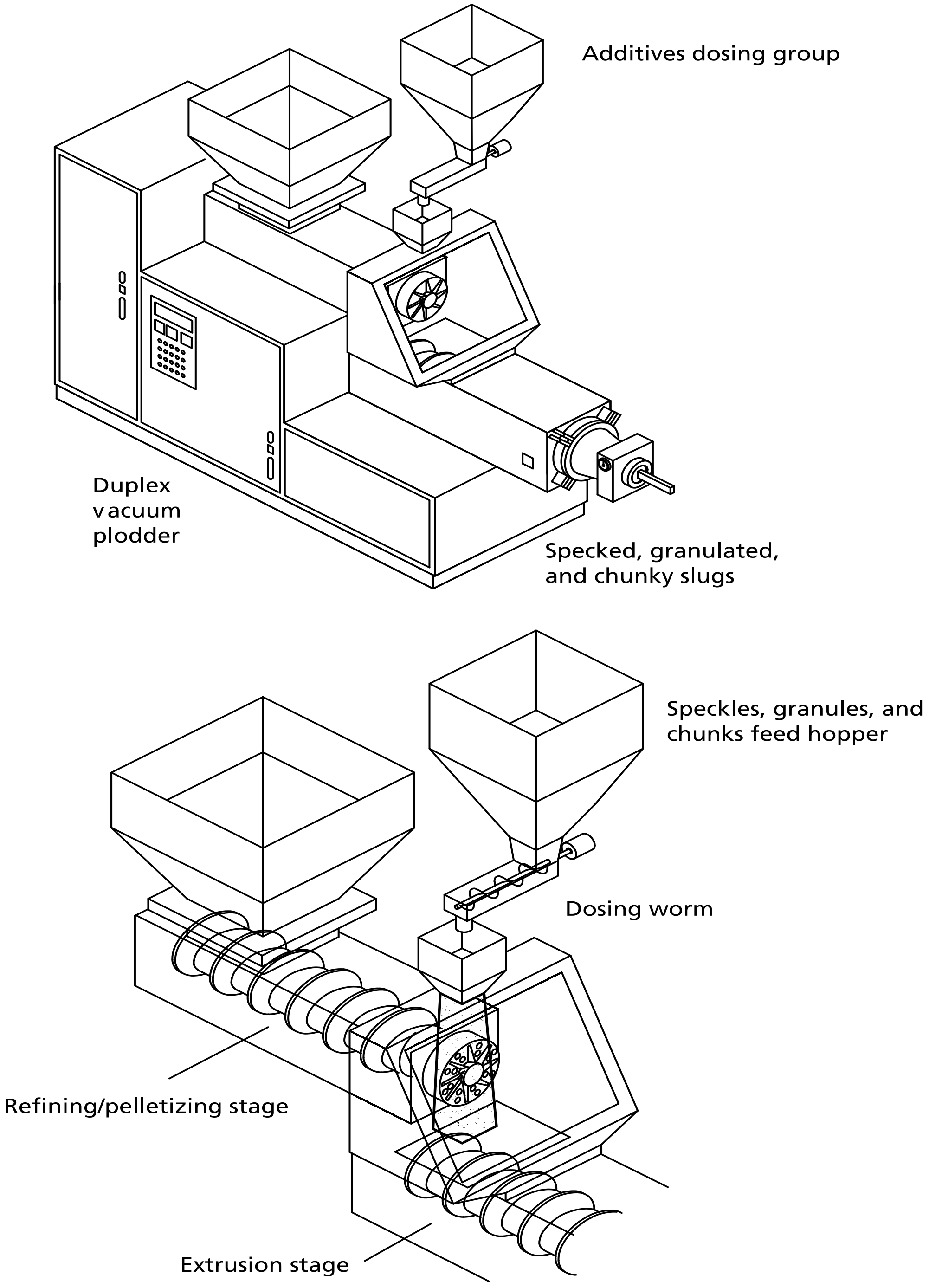


Figure 10.7 Solid–solid system for two-tone soaps—utilizing non-tangential twin-worm plodders.



Figures 10.8 Solid–solid system for speckled soaps—addition into first stage of duplex vacuum plodder.



Figures 10.9 Solid–solid system for speckled soaps—addition into the extrusion stage of the duplex vacuum plodder.

Solid–Solid Co-Extrusion Systems for Marbleized, Striped, and Two-Tone Soaps

To obtain well-defined striped soaps, a co-extrusion system is used that consists of the following:

- A standard duplex vacuum plodder for the primary base.
- A simplex co-extruder plodder for the injection of the secondary base.
- An interconnecting “striping/marbleizing group” with a tube-bundle cylinder: tube bundle, drilled plate, rotor-drive group. This optional group can run the rotor at different speeds than the fixed plodder worm speed, allowing one to obtain a wider range of marbleized effects. The tube bundle has different diameter tubes. The primary base soap is fed through the larger diameter tubes and the co-extruded secondary base, which is always of lesser quantity is fed through the smaller tubes.

Solid–Solid Co-Extrusion System for Marbleized Soaps

This system includes a rotor device for the production of marbleized soaps (Figure 10.10). If the rotor is removed, striped soaps can be made.

Solid–Solid Co-Extrusion System for Striped Soaps

The refined/pelletized primary base from the duplex vacuum plodder is extruded into the tube bundle of the “striping group” assembly. A secondary base co-extruder (simplex plodder) feeds the secondary base into the tube bundle as well. To achieve the striped patterns, the two bases remain separate until they exit from the extrusion head (Figure 10.11).

Solid–Solid Co-Extrusion Group Assembly without Rotor for Striping

This is a complete system including a rotor-drive group (Figures 10.12 and 10.13).

Solid–Solid Co-Extrusion Assembly with Rotor Drive Group for Striping and Marbleizing

See Figure 10.14.

Solid–Solid-Liquid Co-Extrusion Multipurpose System for Striped and Marbleized Soaps

This multipurpose combination system includes all the components of the solid-solid and the solid-liquid systems. (Figure 10.15.)

Solid–Solid Co-Extrusion System for Two-Tone Striped Soaps

This system utilizes a tangential twin-word plodder and a single-worm co-extruder for the production of interesting two-tone striped designs (Figure 10.16).

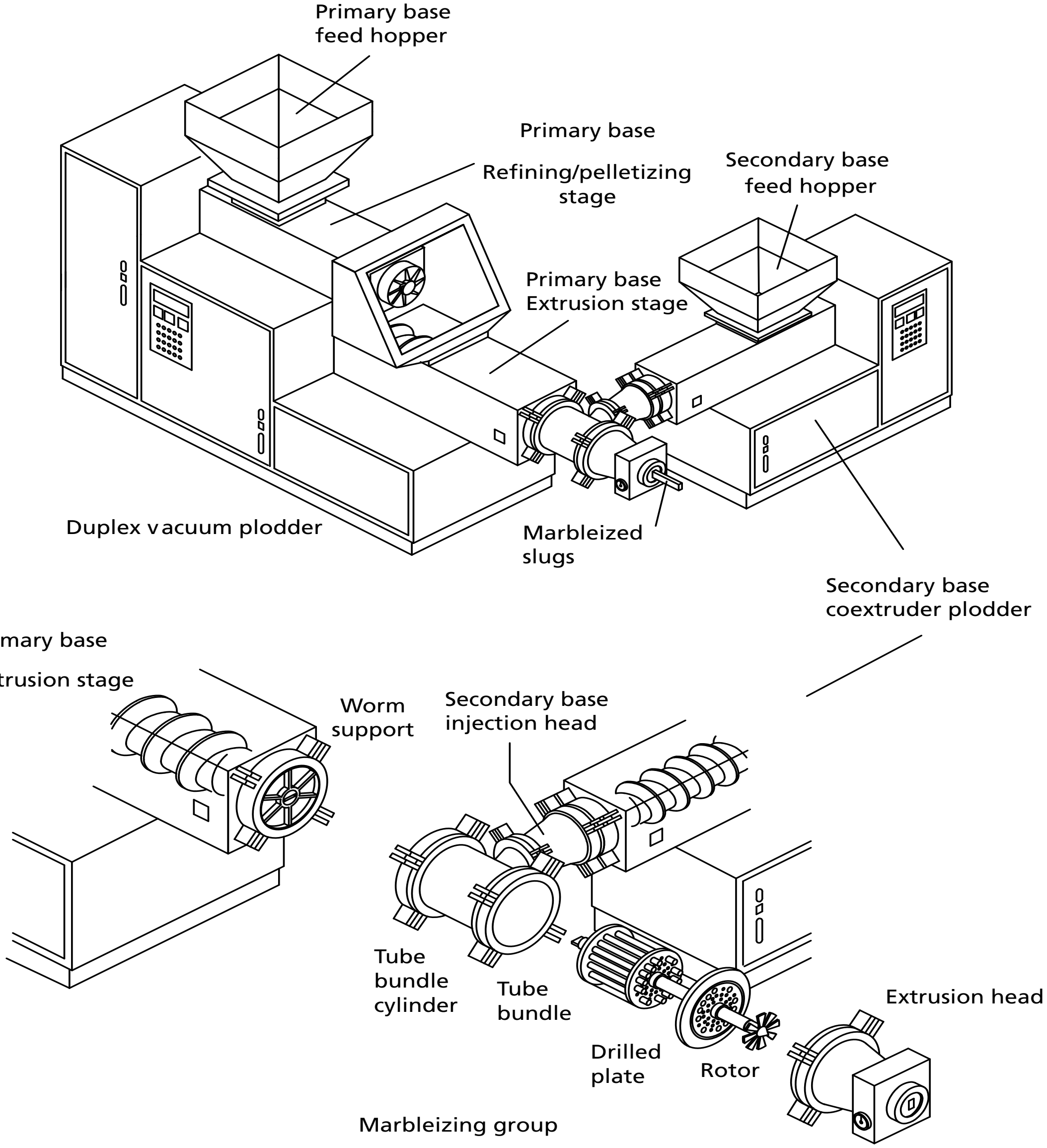


Figure 10.10 Solid–solid co-extrusion system for marbleized soaps.

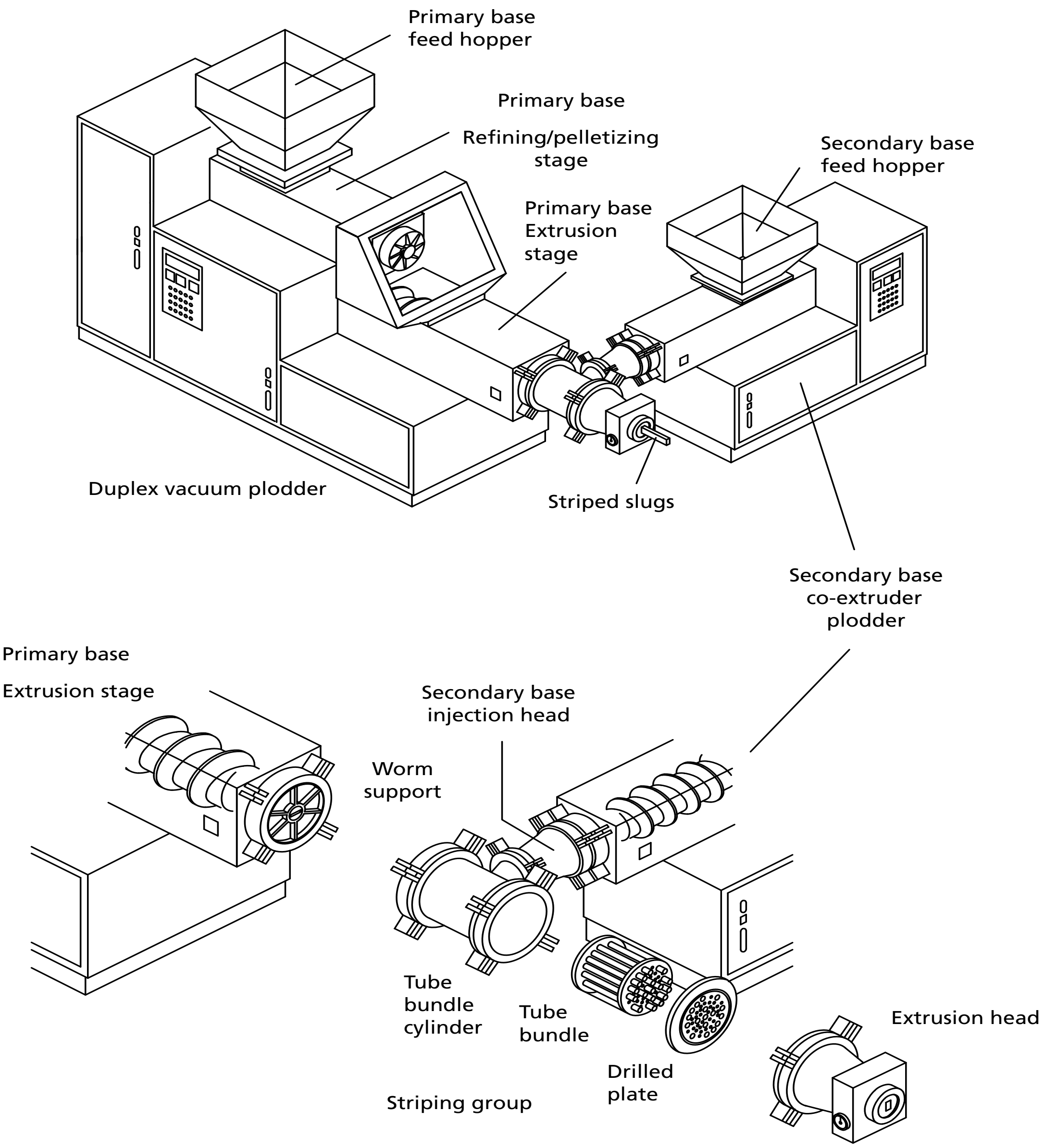


Figure 10.11 Solid–solid co-extrusion system for striped soaps.

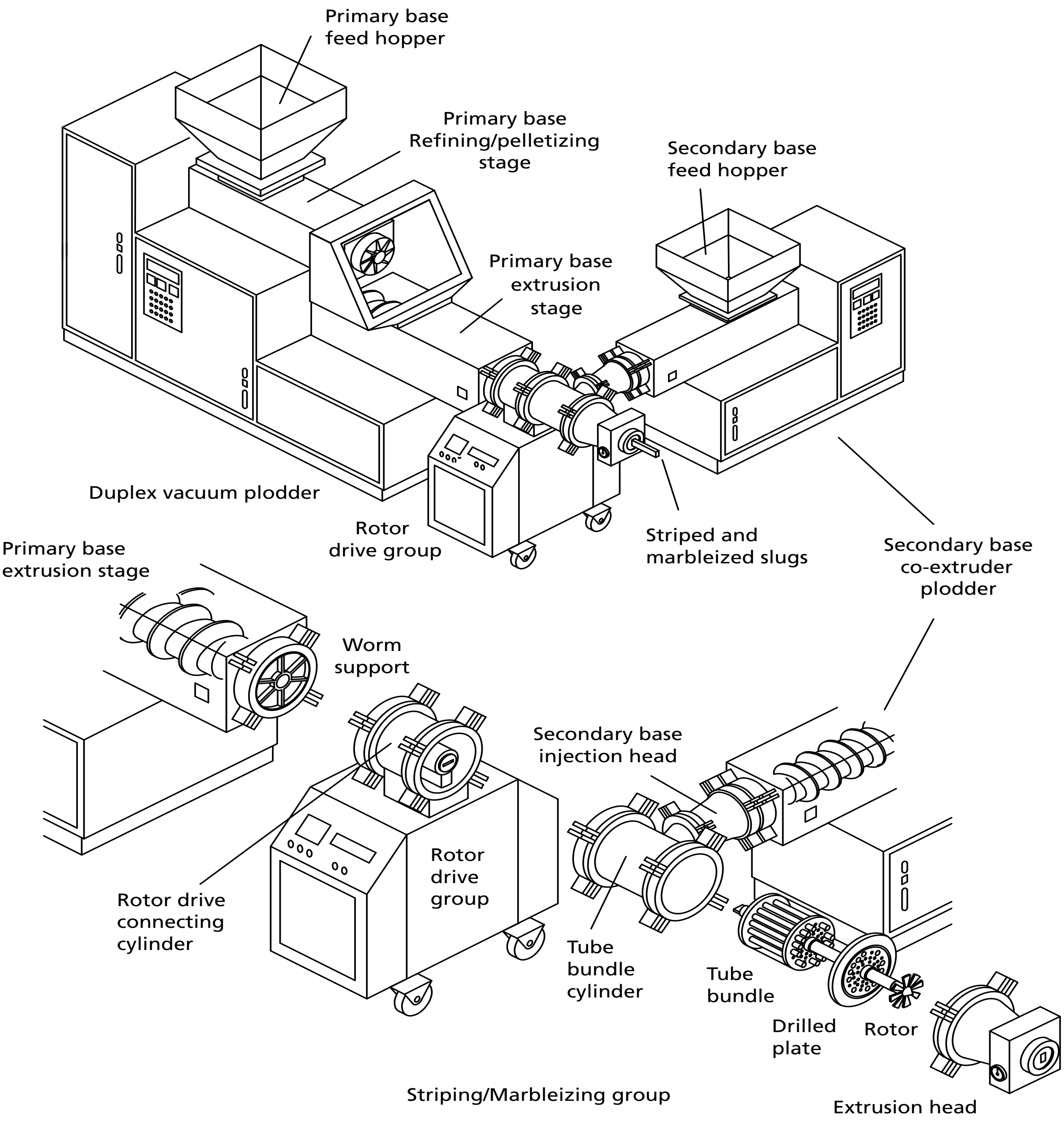


Figure 10.12 Solid–solid co-extrusion system with rotor drive group for striped and marbleized soaps.

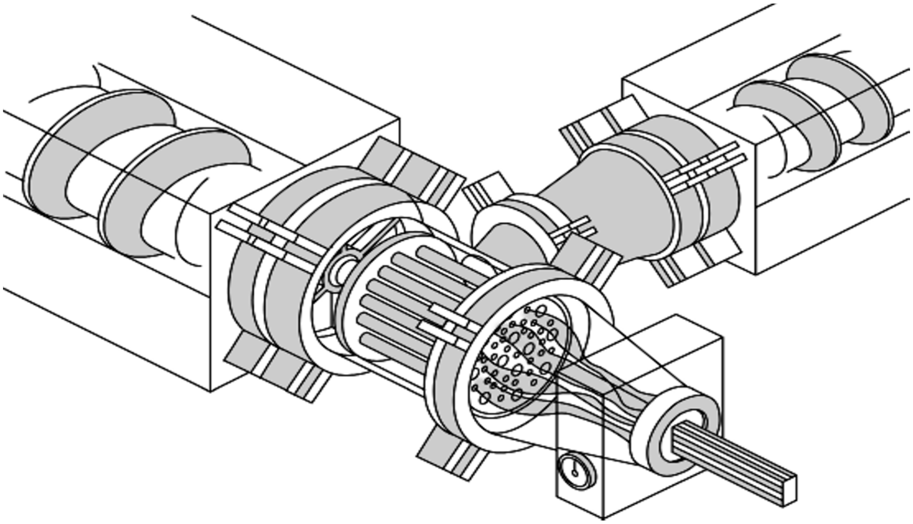


Figure 10.13 Solid–solid co-extrusion assembly for striping.

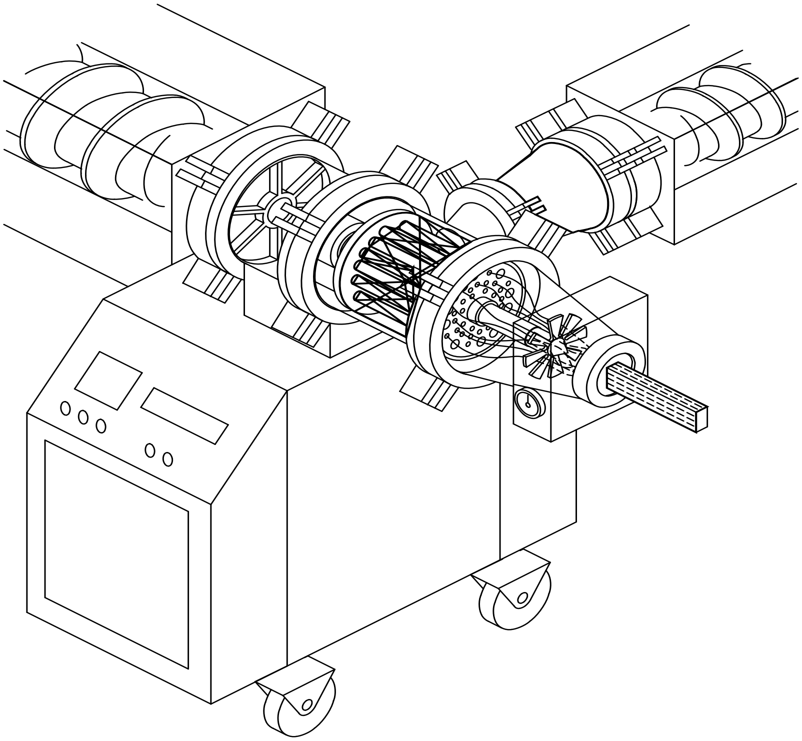


Figure 10.14 Solid–liquid co-extrusion system assembly with rotor drive group for striping and marbleizing.

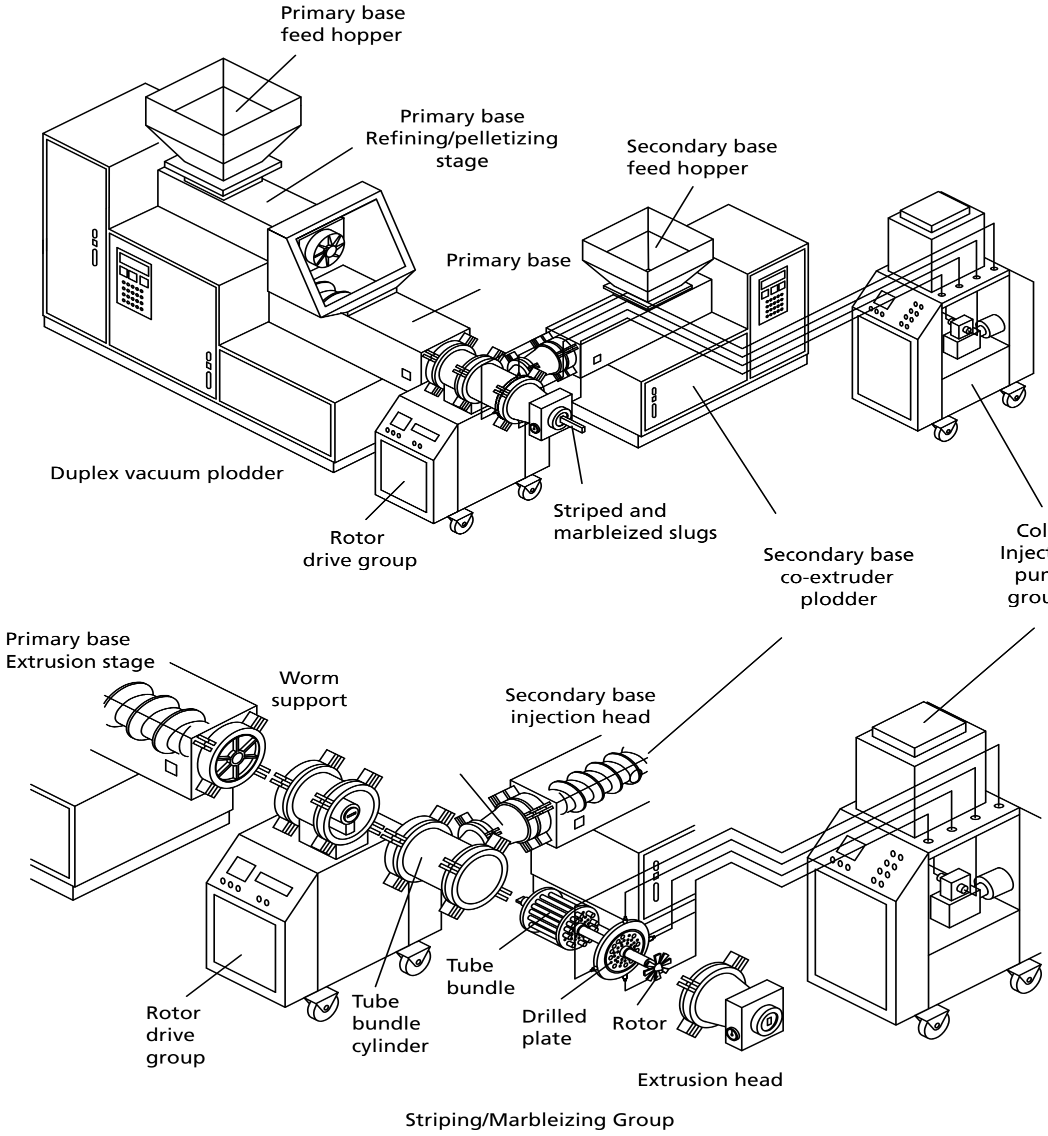


Figure 10.15 Solid–solid-liquid combination multipurpose system for striped and marbleized soaps.

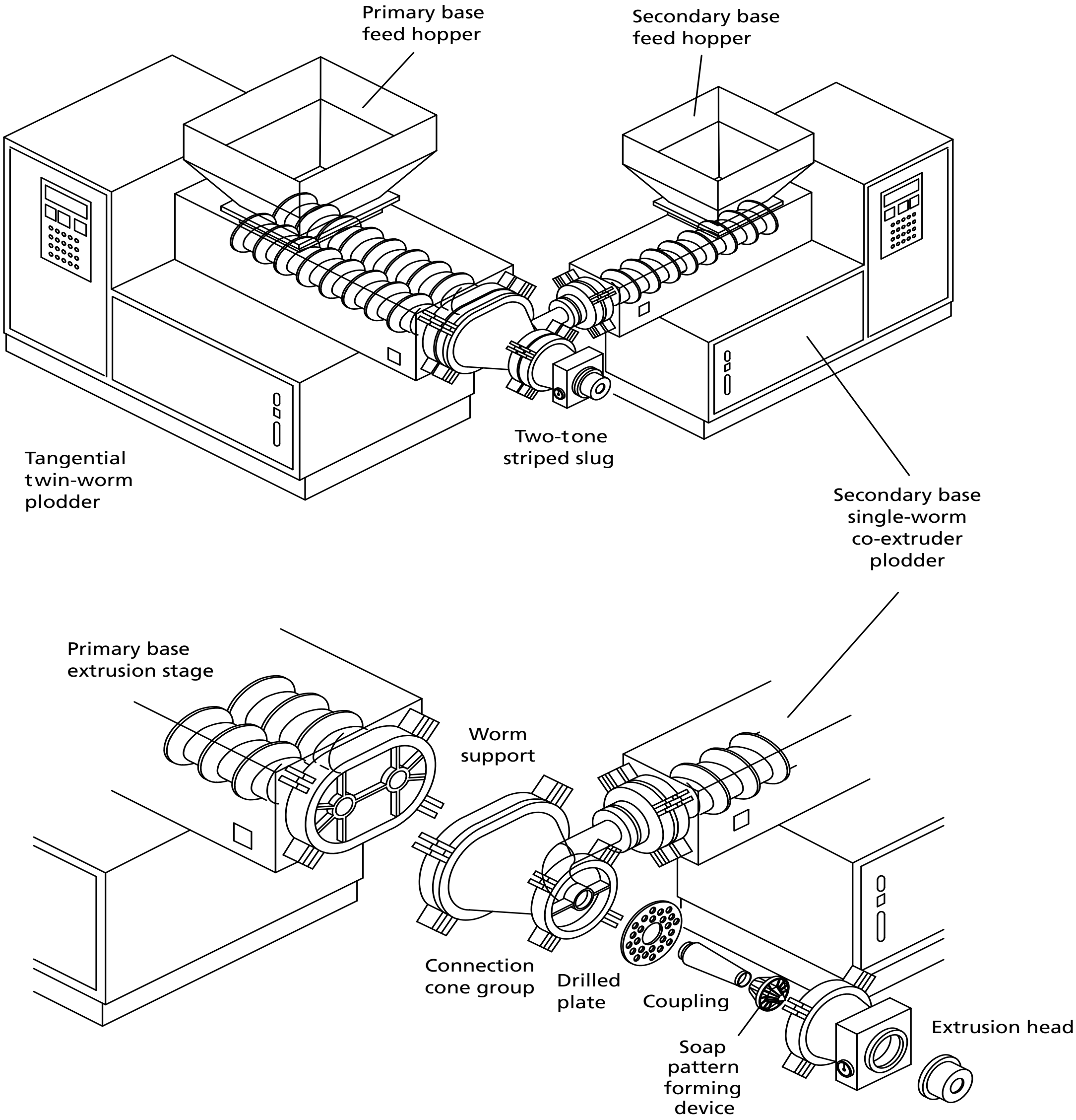


Figure 10.16 Solid–solid co-extrusion systen for two-tone striped soaps with a tangential twin-worm plodder and a single-worm co-extruder.

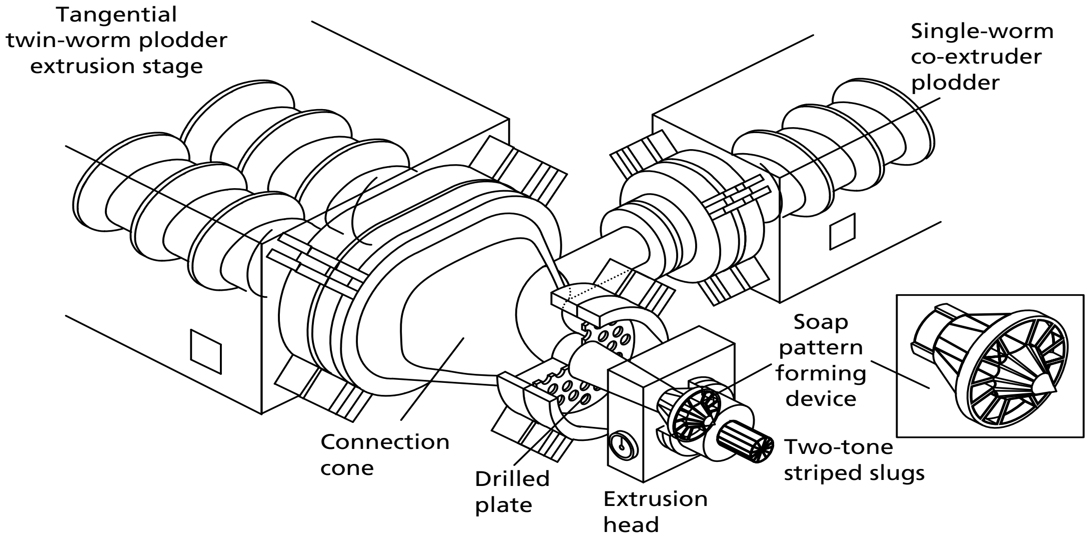


Figure 10.17 Solid–solid co-extruder system assembly for two-tone striped soaps.

Recycling Methods and Stamping Options

To maintain constant multicolored and multicomponent effects, it is essential to control the recycling of:

- Flashing, which is the excess soap formed as the dies meet each other when the flash-stamping system is used for stamping bandless shaped bars
- Excess slugs resulting from extrusion, cutting, and stamping rate synchronization
- Rejected stamped bars from stamping and packaging speed synchronization operation and stamped bar inspection
- Shavings, which are thin pieces moved from the surface of the extruded slugs to expose a better defined inner pattern

Recycling Method for Solid–Liquid Systems

The simplest method is to recycle everything into the first stage of the duplex vacuum plodder. But in this case, no control exists over the total amount recycled, and therefore no control is possible over the final marbleized pattern of the extruded soaps (Figure 10.18).

Recycling Methods for Solid–Solid Co-Extrusion Systems

All items to be recycled are recolored and repelletized in an additional simplex pelletizing plodder and fed into the secondary base co-extruder. Two versions are illustrated in Figures 10.19 and 10.20.

Standard and Angled Bar Soap Stamping Modes

Figure 10.21 illustrates the difference between the straight (standard) and the special angled (bias) stamping modes. Stamping with the dies positioned from 20 to 30 degree angle enhances the appearance of multicolored soaps.

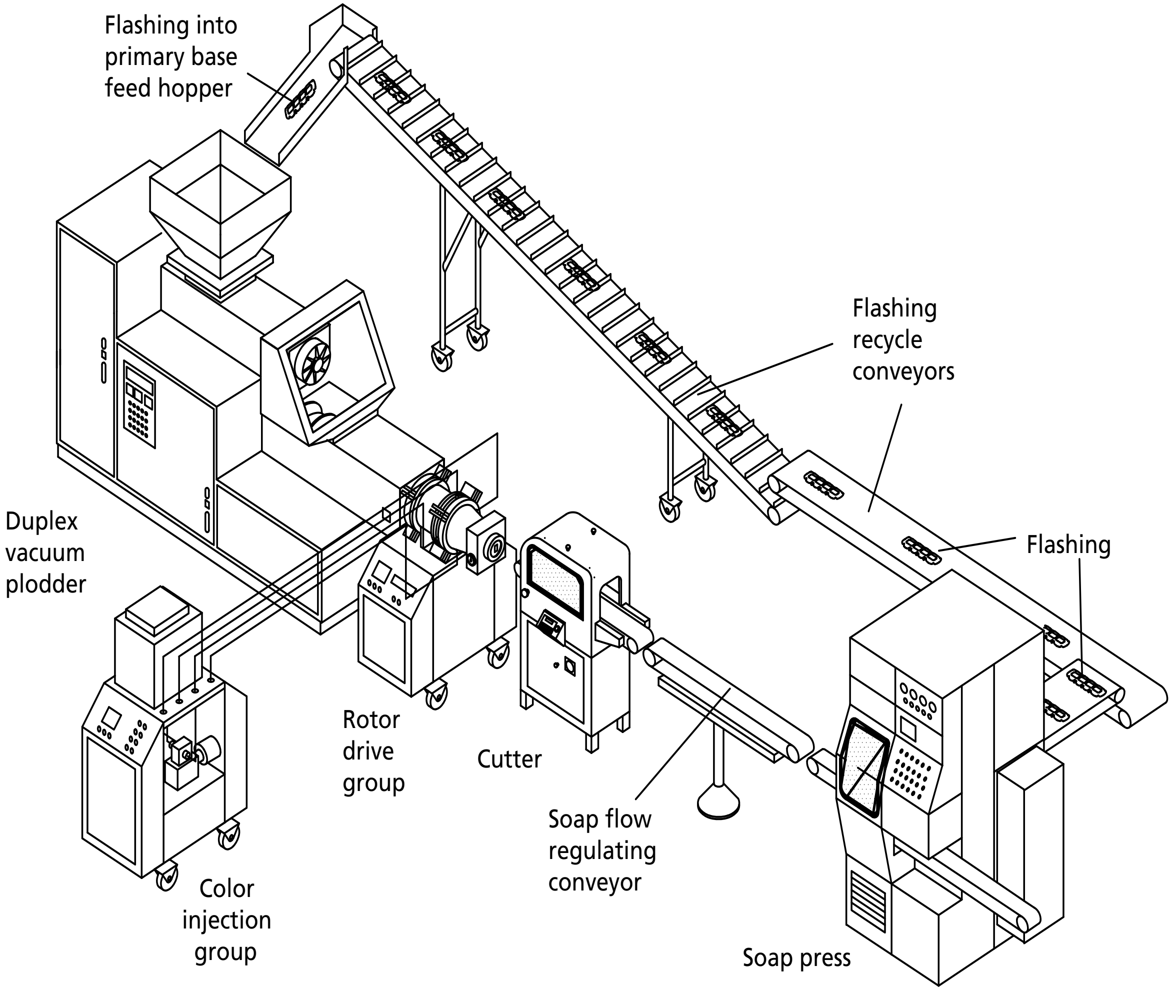


Figure 10.18 Recycle method for solid–liquid systems.

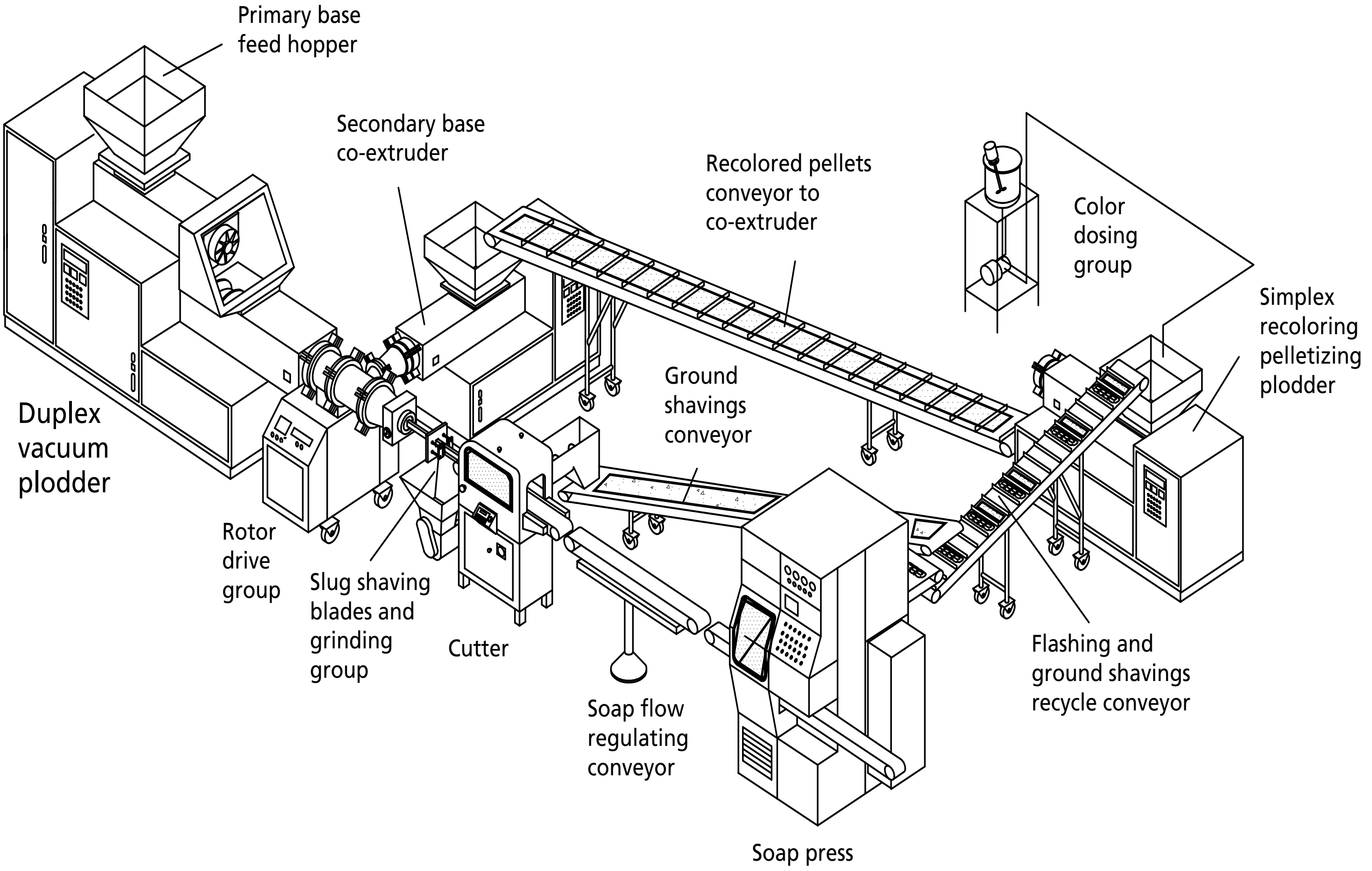


Figure 10.19 Recycle method for solid–solid co-extruding systems—version 1.

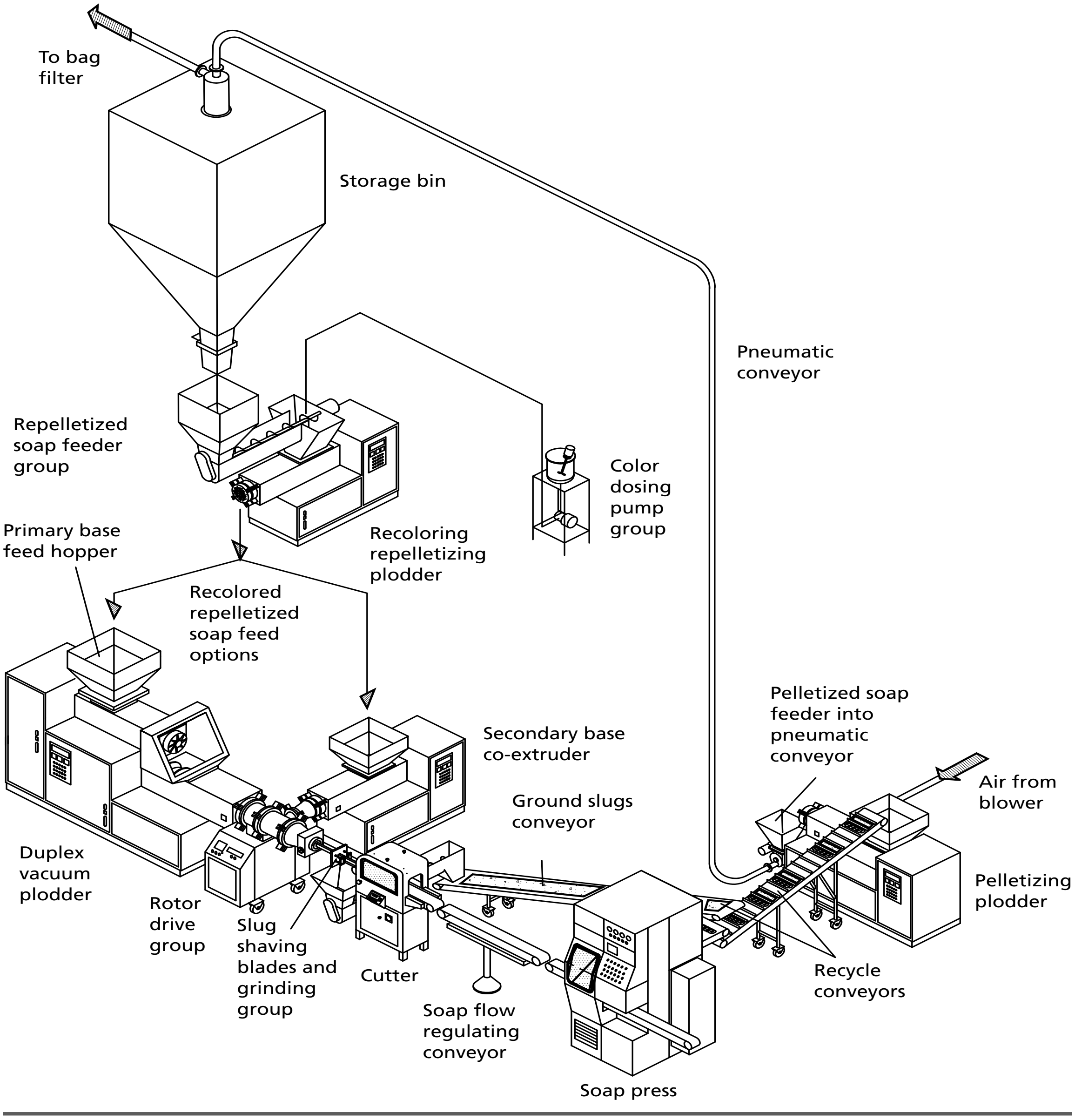


Figure 10.20 Recycle method for solid–solid co-extrusion system—version 2.

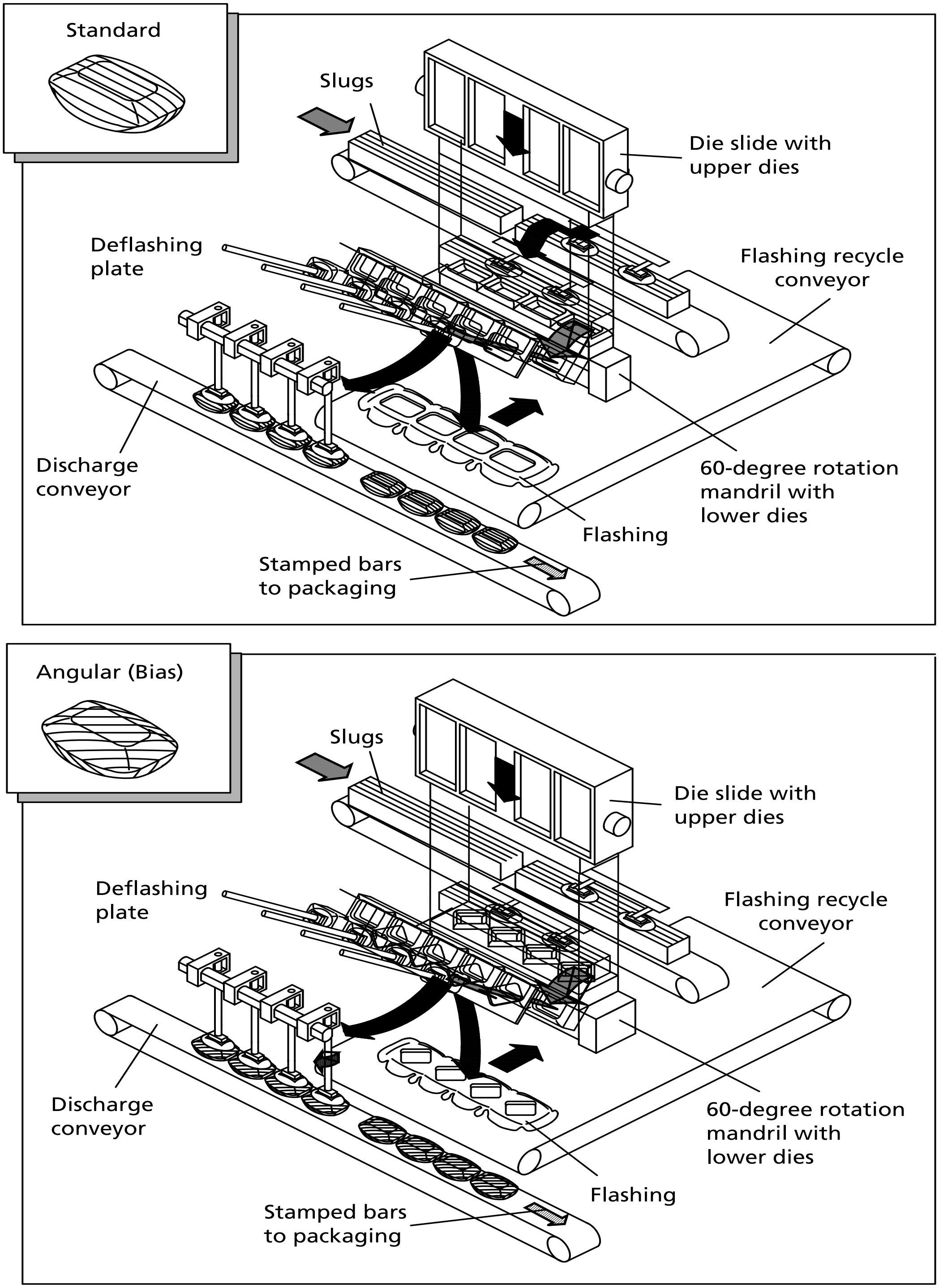


Figure 10.21 Standard and angular bar soap stamping methods.

Acknowledgment

I appreciate the assistance of Mazzoni LB, SpA, for the preparation of the manufacturing system diagrams.

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11 Soap Bar Performance Evaluation Methods

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This chapter surveys the assessment procedures that are practiced in soap bar factories or in development laboratories around the world to ensure that manufacturing standards are met and, ultimately, that consumers will be satisfied with the cleansing bars they purchase. In principle, the appraisal methods include analytical chemistry tests to evaluate raw materials and finished product, methods of materials science to assess product structure, and straightforward tests of the consumer-observable attributes like lather, wet-bar feel, and wear rate, either in the laboratory or by consumer panel assessment. The main focus in this chapter concerns the finished product, although characterization (rheology) of partially manufactured soap is also considered.

Wood has provided a thorough review of many of the common practices of soap manufacturers and of producers of fats and fatty acids for soap makers (Wood, 1990, 1996). Since these methods remain essentially the same, some replication was inevitable.

When discussing evaluation procedures and quality control for soap bars, it should be noted that formal governmental standards for product performance and for methods of testing soap bars exist only in a few countries, namely India, Bangladesh, and Kenya. In these countries, soap is included in the list of items covered by a mandatory certification scheme, which had been introduced with the intention of protecting consumers against substandard, low-quality products on the market. In the rest of the world, consumer acceptance is the only criterion for judging the performance of marketed bars and their commercial success. Consequently, a variety of evaluation procedures are used and have been described in the literature, and each company adopts techniques that meet its particular quality requirements. In the following sections, we survey some of the more common procedures and, where applicable, include for comparison the standard tests of bar performance mandated by the Bureau of Standards in one of the above-mentioned three countries where such standards exist.

Lather Evaluation

An adequate instrumental evaluation of the lather or foaming properties of soaps is not simple, due to the complex nature of the lathering process. Many lather attributes, such as speed of generation, volume, bubble size, and stability, contribute to the overall consumer perception of lather, and these attributes are also greatly affected by the manner in which the lather is generated. Numerous evaluation techniques and devices to generate lather have been described in the literature to date. One of the techniques, proposed by J. Ross and G. Miles in 1941 (1941) and now commonly referred to as the Ross-Miles foam test, measures the height of foam developed by pouring. It eventually became a standard test method for foaming properties of surface active agents (ASTM International, 2007). Though quite suitable for detergent solutions, this method does not differentiate well between soap bar products or provide a reliable correlation with the consumer perception of lather; consequently, many soap manufacturers developed a variety of other evaluation techniques.

The amount of lather generated by a soap bar is an important parameter affecting consumer acceptance and preference. According to the Bureau of Indian Standards, the lather requirement is intended to ensure the presence of an adequate level of surfactants in the bar for cleaning. The Indian Standards prescribe the following procedure for the determination of lather (Bureau of Indian Standards, 1983, 1992): a sample of 5 g uniformly grated (to about 0.5–2 mm size) soap is added to 100 ml of 300 ppm hard water in the blending jar of a kitchen food blender. The jar is covered and the blender is set on low speed for exactly 60 seconds. Then the lather is poured quickly into a graduated cylinder and measured immediately after leveling off the top surface of the foam. This method must be calibrated (by adjusting the speed of the blender) so that when the blender is operated for 60 seconds, it delivers 600±100 ml of lather from 100 ml of a 1% sodium lauryl sulfate solution at an ambient temperature of 27±2 °C. The measurements should be performed on three samples with three duplicates, and the result is reported as the mean x (the sum of test results divided by the number of test results) and the range r (the difference between the maximum and the minimum values of the test results). In India, bars are deemed to conform to the standard requirements of a particular grade if the expression $(x - 0.6r)$ is greater than or equal to 280 ml for grade 1,240 ml for grade 2, and 200 ml for grade 3, respectively.

Another common lather evaluation technique often described in the patent literature is the conventional sudsing test (Wood, 1990), also referred to as a cylinder test, which is conducted by dissolving a specified amount of soap in de-ionized water, placing an aliquot of this solution into a graduated cylinder with a stopper, and shaking the cylinder. The net volume of the foam can be read directly, and also the stability of the foam can be measured by monitoring the foam height as a function of time. Typical specifications for this procedure are as follows: the soap solution (suspension) concentration is 1% wt.; the cylinder volume is 250 ml, wherein 50 ml of the solution is placed and the cylinder shaking is performed by inversion via rotating cylinders at several revolutions per minute for a total of about 30 inversions. A variety of modifications of this test, with adjustments to meet particular requirements, may be used. Figure 11.1 shows a simplified version of a cylinder test, conducted by hand-shaking 100-ml cylinders filled with 10 ml 1% solution of two different soap bars. This provides a direct comparison of the foam volume (height), and one can also monitor the rate of foam drain by measuring the volume of the drained liquid at the bottom of the cylinder.

Recently, a new automated mechanical foam tester, SITA Foam Tester R2000, has been introduced to the market (SITA Messtechnik GmbH, 2008), and it offers easy and repeatable testing and monitoring of the foaming characteristics for foaming liquids. It provides fully automated control of the test algorithm (measuring, cleaning, and refilling), reproducible test results, various settings for the test parameters, and automatic self-cleaning using tap water after completing an experiment.

A common feature of all tests described above is that a prepared solution or suspension of a soap bar is used to generate lather. The step of manipulating a soap bar in the hands (at the sink or in the shower), which is an essential factor in the process of soap dissolution and lather generation, is missing, and, therefore, these tests seem to be less

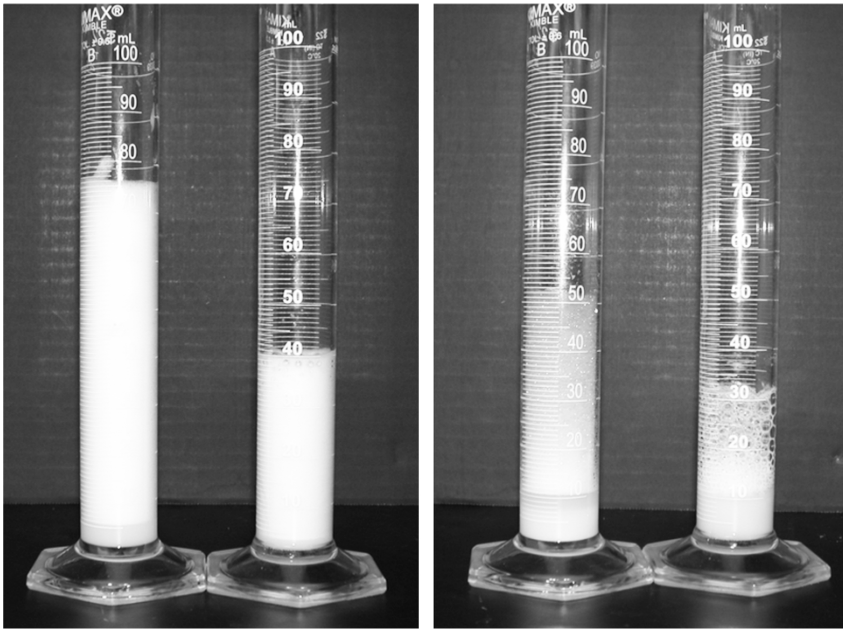

Figure 11.1 Foam generated in a cylinder hand-shake test from a syndet (left) and a regular soap (right) bars: (a) initial volume; (b) after 2 hours.

suitable for bars than for liquid detergents. Consequently, in order to better simulate the in-use conditions, and achieve a better correlation of in-lab appraisals with the consumer perception of lather in the shower, a number of tests have been developed involving generation of lather in the hands by a trained technician.

In order to obtain an objective comparison of different soap formulations (and also good reproducibility and consistency between different appraisers), the lather tests are conducted using a standardized protocol under a set of strict conditions. A subjective assessment of lather creaminess is made by a technician during the generation of the lather.

The lather appraisal procedure is typically as follows (Yarovoy, 2003):

1. Tablet pretreatment: Wearing disposable gloves, worn inside out and well-washed in plain soap, wash down all test tablets for at least 1 minute before starting the test sequence. This is best done by twisting them about 20 times under running water.
2. Place about 5 liters of water of known hardness and at a specified temperature (typically 20–40 °C) in a bowl. Change the water after each bar of soap has been tested.
3. Take up the tablet, dip it in the water, and remove it. Rotate the tablet 15 times between the hands. Replace the tablet on the soap dish.

The lather is generated from the soap remaining on the gloves:

- *Stage 1:* Rub the tips of the fingers of one hand (either hand) on the palm of the other hand 10 times.
- *Stage 2:* Grip the right hand with the left, or vice versa, and force the lather to the tips of the fingers. Repeat with the hands reversed. This operation is repeated five times with each hand.

Repeat Stages 1 and 2.

1. Place the lather in the calibrated beaker.
2. Repeat the whole procedure of lather generation twice more, combining all the lather in the beaker.
3. Stir the combined lather gently to release large pockets of air. Read and record the volume.

Another common evaluation technique involving generation of lather in the hands is usually referred to as an inverted-funnel method (Farrell & Nunn, 2005). It requires a large measuring funnel and two large sinks. The measuring funnel is constructed by fitting a 10½-inch-diameter plastic funnel to a graduated cylinder that has had the bottom cleanly removed. The graduated cylinder should be at least 100 cc. The fit between the funnel and the graduated cylinder should be snug and secure. Before evaluations proceed, place the measuring funnel into one of the sinks and fill the sink with water until the 0 cc mark is reached on the graduated cylinder. The procedure involves the following steps, some of which are illustrated in Figure 11.2:

1. Run the faucet in the second sink and set the temperature to 95 °F (35 °C).
2. Holding the bar between both hands under running water, rotate the bar for 10 half-turns.
3. Remove hands and bar from under the running water.
4. Rotate the bar 15 half-turns and lay the bar aside.
5. Work up lather for 10 seconds.

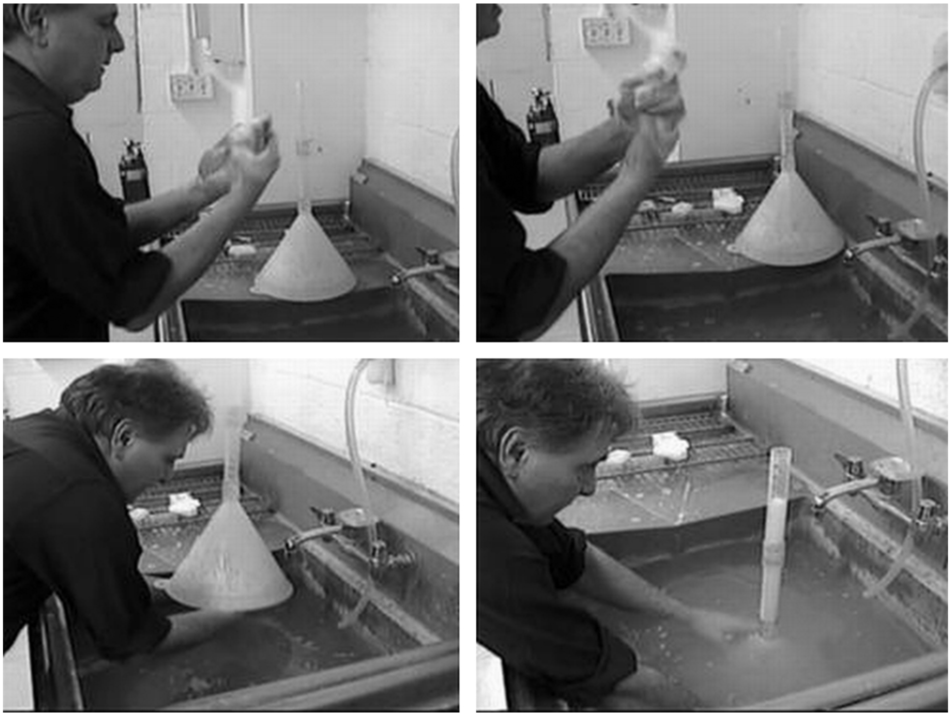

Figure 11.2 Foam appraised by a technician using an inverted-funnel test.

6. Place funnel over hands.
7. Lower hands and funnel into the first sink.
8. Once hands are fully immersed, slide out from under funnel.
9. Lower the funnel to the bottom of the sink.
10. Read the lather volume.
11. Remove the funnel with lather from the first sink and rinse in the second sink.

The test should be performed on several bars, and the volume should be reported as an average.

When the goal of an appraisal is to compare lather of a new bar prototype with the control, a paired-comparison protocol is used for the data analysis, which involves calculating a value of least significant difference (LSD). Typically, six results for each bar are averaged, and paired comparisons are carried out between the averaged results for each bar. If the lather volume differs by more than the LSD, then the products are said to produce "significantly different amounts of lather."

Rate of Wear and Mush

After lather, the rate of wear (ROW) is one of the most important soap bar properties, especially in developing countries, where a purchase decision is often strongly influenced by a soap bar economy or a value-per-dollar consideration. A laboratory evaluation of the ROW is a relatively straightforward test performed by washing a bar multiple times and measuring the bar weight loss after the final wash. The ROW is usually reported as the bar mass loss (in grams) per wash. When comparing the ROW of bars having different weight, the ROW values should be normalized to a 100 g bar weight, or expressed as a percentage of the bar weight. The ROW often correlates strongly with mush—high mush scores usually signal a high ROW.

Even though this procedure appears to be straightforward, a variety of nuances have been introduced in order to better correlate the laboratory data with consumer perceptions. This is illustrated below by three test descriptions, randomly selected from the patent literature, which are presented in the order of increasing complexity.

Version 1: Wet a pre-weighed bar in running water and rotate 15 times while in the tester's hands. Place on a support stand. Repeat 10 times at half-hour intervals. Weigh the washed bar after allowing to dry at room temperature for 16 hours. The weight change multiplied by 100 and divided by the initial weight of the bar denotes the percent rate of wear of the bar (Abbas & Hui, 2004).

Version 2: The evaluation is carried out over a 4-day period in order to simulate at-home usage (Subramanyan et al., 1996). The initial weights of the bars are recorded. A few different individuals wash the bars for 10-second intervals in warm tap water, 32–38 °C. The soap bars are placed in a soap dish with a grid to allow drainage of water. The bars are allowed to dry for at least a 30-minute interval between washings. The soap bars undergo a total of 20 washes of 10-second duration, and then are dried for 24 hours prior to reweighing. The results are reported as a weight loss per 100-gram bar per one use.

Version 3: In this test, water is added to a soap dish to induce the formation of mush. Weigh the bar to be tested. Set up an 8-liter bucket with continuous water running through it at 40.5 °C. Immerse the bar into water, remove, and then rotate it in the hands 20 times. Repeat. Immerse the bar again to remove adhering lather, place in a dish, and dry in the air at 25 °C and approximately 50% RH. Repeat every 2 hours over an 8-hour span. Let dry for 12 hours at 25 °C and approximately 50% RH in a dish, and repeat for another 8-hour span. Add 10 g of de-ionized water to the dish between immersions and while the bar is resting in the dish. This should be additive over the 8-hour span: after the first 2 hours, 10 g water are added to the dish; after 4 hours, add 10 g more, totaling 20 g water in the dish; after 6 hours, add 10 g more, totaling 30 g water in the dish; and so on, for the 8-hour period. Then dry for 12 hours. The weight of the bar after 12 hours is recorded, and the wear rate is the percent weight loss of the bar (Brennan et al., 2008).

Closely related to the rate of wear is the propensity of most soap bars to form a soft, loose layer on the surface when in contact with water for a prolonged period of time (several hours). During subsequent use, this layer is readily washed down, contributing to both the generation of lather and the bar wear. In the patent literature, one finds different terminology used to describe this phenomenon. For example, Cussons and Unilever denote it as "mush" and "mushing," Procter & Gamble uses the term "smear," and Colgate refers to it as "slough." Excessive mush is disadvantageous because it represents a loss of soap from the bar and typically leads to greater rates of wear.

There are two somewhat different ways to generate and appraise mush in a laboratory environment: (1) soaking a bar in a dish and (2) immersing a suspended bar in water.

Procedure 1: In the first procedure, a bar is placed in a small dish, 30 g of water are added, and the bar is soaked for 24 hours. Then the mush layer is gently scraped with a blunt blade. The weight W_m of the mush layer is measured and divided by the initial weight W_i of the bar prior to soaking to obtain a mush weight fraction, $x_m = W_m/W_i$. The final weight of the bar W_f after the mush layer has been scraped off is also measured. The water uptake weight fraction x_u can be calculated as $x_u = (W_m + W_f - W_i)/W_i$. Three bar samples of a formulation are typically evaluated in this manner, and the average x_m and x_u are reported (Post et al., 1998).

Procedure 2: In the second procedure, a bar is shaved to the dimensions 7 cm × 4 cm × 2 cm, and a line is carved halfway down the center of the bar (at the 3.5 cm mark). Then half of the bar (to the line) is suspended in de-ionized water for 2 hours at a temperature of 25 °C. After this time, the bar is removed, water is drained for 30 seconds, and the bar is weighed. This is the weight of the bar, the mush, and the absorbed water. After weighing, the mush is scraped from the bar, and the bar is dried for 12 hours. The difference in weight between the initial dry bar and the final dry bar, calculated for the 50 cm^2 bar surface area, is the amount of mush (grams). The difference in weight of the soaked bar and the initial dry bar is the amount of water absorbed (Brennan et al., 2008).

A variety of modifications of these techniques exist. For example, the soft layer may be removed by hand rather than spatula, the soaking time (in dishes) decreased to 17 hours, and the temperature of soaking increased to 35–40 °C (Subramanyan et al., 1996; Colwell & Pflug, 1991). The weight loss due to mush formation in this test is reported as the loss per 100 grams. The Kenya Bureau of Standards recommends a modified version of the first procedure (tested bars are placed on wet fabric instead of in dishes with water), whereas the second procedure is adopted in India as the standard.

The mush (or smear) can also be graded using a subjective scale by a trained technician who grades soap bar smear by fingering the bar and taking into account both types of smear and amount of smear. Such a test is typically carried out as follows: (1) place a soap bar on a perch in a 1400-mm-diameter circular dish; (2) add 200 ml of room-temperature water to the dish such that the bottom 3 mm of the bar are submerged in water; (3) let the bar soak overnight (15 hours); (4) turn the bar over and grade qualitatively for the combined amount, characteristics, and depth of smear on a 1 to 10 scale, where 10 equals no smear, 8.0–9.5 equals low smear amount, 5.0–7.5 equals moderate smear similar to most marketed bars, and 4.5 or less equals very poor smear (Kacher, 1995).

Wet Cracking

Wet cracking, or cracking of soap bars during repeated usage, is a well-documented phenomenon that occurs when faults in the macro- and microstructure are stressed during bar/water interactions. Many factors affect the development of cracking: the composition of the soap, the efficiency of the soap finishing line (the degree of compaction during extrusion), and the bar shape.

A generic procedure for evaluating wet cracking comprises the following steps: (1) soaking a bar by full immersion in water for a prescribed period of time at a constant temperature, (2) draining the water and drying for 16–24 hours at the soaking temperature, (3) visual evaluation by comparing to a set of photographs or illustrations (Marchesani, 1979). Figure 11.3 illustrates a possible set of photographs for rating both face and end cracking on a six-point scale (from 0 to 5) (Geoffrey, 2005), with zero being no cracking and five representing very severe and unacceptable cracking.

Various modifications of this generic procedure exist. For example, more recent Colgate patents (Colwell & Pflug, 1991) provide the following details for the wet cracking test: soap bars were suspended in tap water at room temperature (24 °C) for 4 hours, then allowed to dry for 24 hours prior to being evaluated. Any resulting cracks on the bar surface were rated numerically using a scale of zero (none) to five (severe), and then summed. For example, a soap bar having five cracks of severity one, plus two cracks of severity four has a total rating of 13. A total rating of more than 25 is considered unacceptable. Shorter immersion times, such as a half hour or 1 hour, may be also used, and the resulting cracking may be reported on a scale from zero to five (Sonenstein, 1981).

The number of cycles of wetting and drying may also be changed, and a new step, rinsing, may be introduced to simulate in-use conditions more closely. For instance, Hyeon (2005) describes a test in which a bar was dipped in tap water at 30 °C for 2 hours. After soaking for 2 hours, the swelling part was removed from the soap and slightly washed with flowing cold water. Then, the bar was dried at room temperature for 1 hour. After this sequence was repeated three times, the bar was dried for 24 hours in a thermostat at 30 °C and rated for cracking.

Wet-Bar Feel

Wet-bar feel is what the consumer would experience during use of the bar at the sink or in the shower. A bar washdown test is intended to uncover any defects on the bar surface that would feel like grit, sand, or roughness. The average consumer is quite sensitive to bar surface quality and reacts negatively to even minor defects. The wet-bar feel test, or determination of grittiness, is a mandatory test that bars should pass to be certified by the Indian Bureau of Standards, which mandates the following test procedure. Hold the bar under running water at 30 °C and rub the two sides of the bar gently on the palm for one minute. The bar shall show no rough surface and shall feel smooth to the touch. Allow this bar to dry in the open air for 4 hours and examine the surface. Bars pass the test if no gritty

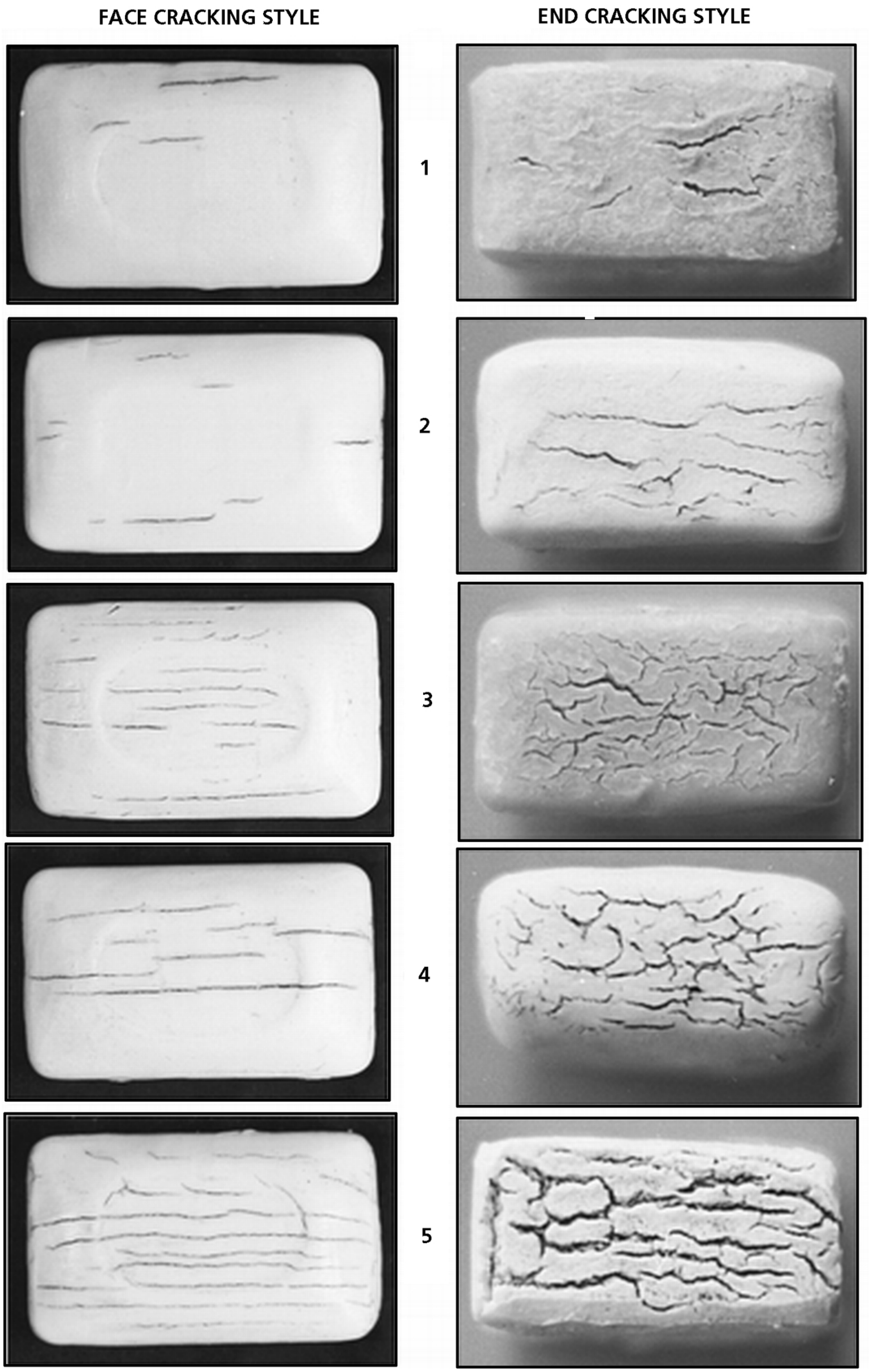

Figure 11.3 Bar wet-cracking visual scale.

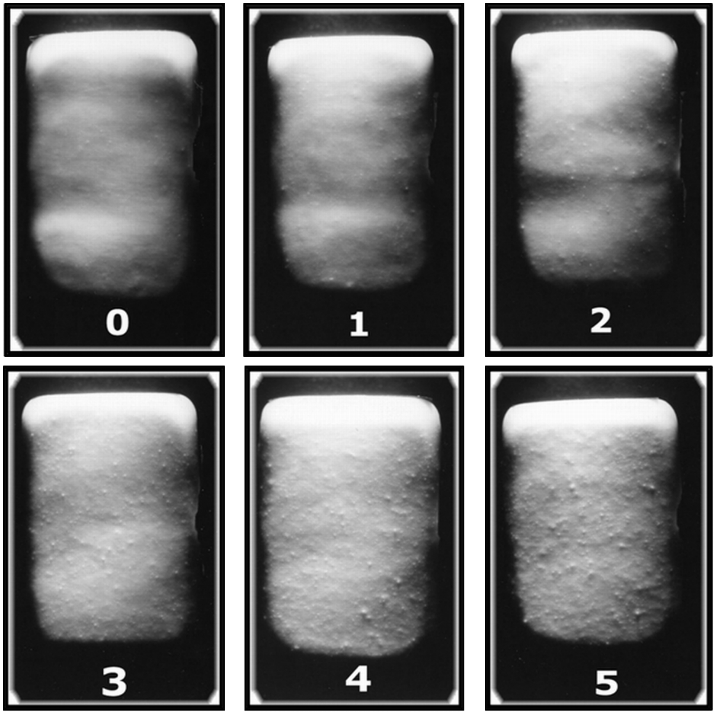

Figure 11.4 Visual scale of bar grittiness.

particles are visible on the surface. Figure 11.4 illustrates the visual grades of bar surface grittiness that can be appraised on a scale from 0–5.

Because the wet-bar feel is a tactile (rather than visual) property, a set of bars molded from plastic having various levels of surface grittiness and/or sandiness could also be used to calibrate the grading scale by touch. Such a reference scale is useful in product development and factory quality control.

Another wet-bar property that could be evaluated during washdown is bar slip (alternatively called drag). In materials science terms, wet-bar feel is a measure of the friction between the product and the skin, and this could be evaluated with friction testing equipment already used for skin tribology (Sivamani, 2003). However, we are unaware of any practical implementation of this type of measurement involving soap bars, and it is reasonable to assume that wet-bar feel, like most consumer traits, is best assessed by asking consumers directly if they find this aspect of the product appealing. Consumer panel assessments are discussed in the User Panel Evaluations section.

Mildness to Skin

It is well known that frequent use of a regular soap (as well as other cleansing products) may result in increased skin dryness and tautness, especially when applied to the face during the cold and dry season and in individuals with dry, sensitive skin. The full potential of a cleansing product to dry and irritate the skin can be assessed in vivo in various clinical tests and in vitro using a number of laboratory assays. Since the clinical tests are usually expensive, it is a good strategy to initially screen the products using in vitro methods.

One of the most common mildness assays is the zein test, which evaluates the effect of soap on proteins by measuring the solubility of the water-insoluble corn protein, zein, in a solution of the cleansing base. Goette (1967) and Schwuger (1969) have shown that a surfactant's ability to solubilize zein correlates well with the surfactant's irritation potential. The lower the zein score, the milder the product is considered to be. A typical procedure involves measuring the percent of dissolved zein as follows: (1) prepare 30 g of 1% cleansing base solution; (2) add 1.5 g zein and mix for 1 hour; (3) centrifuge for 30 minutes at 3000 rpm; (4) extract the pellet, wash with water, and dry in vacuum for 24 hours or to a constant weight; (5) measure the weight of the dry pellet. The percent of zein solubilized is calculated using the following equation (Post et al., 1998; Fujiwara, 1999):

$$\%\ \text{zein solubilized} = 100 \times [1 - (\text{weight of dried pellet} / 1.5)]$$

Final assessment of the mildness of the soap may be conducted using the forearm controlled application technique (FCAT), which is an industry standard method for estimating the relative irritation potential of personal cleansers (Ertel, 1995). This test is usually conducted by independent, certified laboratories. The FCAT uses an exposure protocol that is based on consumer washing habits and a number of instrumental techniques (such as skin conductivity and transepidermal water loss), coupled with visual observations of dryness and redness (erythema), in order to assess the condition of the skin before, during, and after washing.

A detailed review of the effect of cleansers on skin has recently appeared in a special journal issue (*Dermatologic Therapy*, 2004).

Fragrance

Although perfume does not contribute to the cleansing function of soap, it is an important factor in attracting consumers, reinforcing a product image, and reinforcing subjective judgments of product performance (Ho, 2000). One important function of perfume is to mask the base odor that comes from the raw materials. This function can be assessed only by a human expert panel (usually in fragrance houses). Another function is to provide a pleasant olfactory experience during and after soap use. This is closely linked to the release of perfume from soap during the shower, perfume retention in a soap bar over time, and the perfume's ability to deposit on the skin. All of these can be evaluated using headspace analysis, in which vapors are trapped and then analyzed using conventional gas chromatography–mass spectrometry (GC-MS) analysis. A recent technique that has achieved widespread use in analytical laboratories is solid phase micro-extraction (SPME) that eliminates the need for organic solvents and complicated apparatus. In this technique, vapors are trapped on a fine fiber before being directly injected into GC-MS. More details on this technique can be found elsewhere (Smith, 2004).

A typical procedure for evaluating the fragrance headspace using the SPME technique is as follows (Zhou, 2006). A soap bar is placed into a jar and covered by a polyethylene film. Following the incubation period, a preconditioned 100 μm PDMS fiber is inserted into the jar to carry out the headspace extraction for 30 minutes. After extraction, the analysis is performed using GC-MS. Details on the GC column and desorption temperature depend on the type of the GC-MS instrument used.

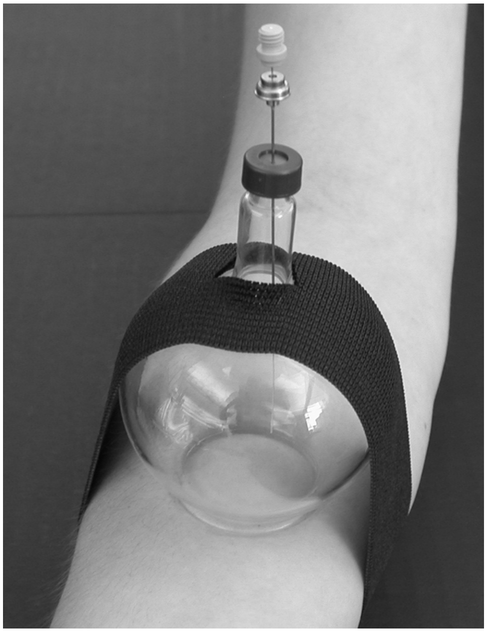

Figure 11.5 Evaluation of the fragrance substantivity using SPME.

This procedure can be applied to measure the headspace over the whole bar, a bar slurry, or diluted solutions (to evaluate the release of fragrance during wash), or over the skin to assess the perfume substantivity after wash. Figure 11.5 illustrates the latter test, in which a microfiber absorbing the perfume is seen inside a glass container covering the area of the forearm skin washed with the bar being tested.

User Panel Evaluations

Product testing with trained (expert) or untrained panelists is also relevant to our discussion of bar soap appraisal. Major consumer products companies use consumer panels or expert panels of appraisers at one or more stages of product development. Panels comprising several hundred people may be used to confirm that a new prototype meets the criteria for launch in the market. Expert or untrained panel appraisals at early and intermediate stages often help direct formula development, and their use is worthy of discussion here because it is often employed to assess one or more of a product's sensory characteristics that are not easily quantified by an instrumental technique.

Characteristics like lather volume, mush, wet-bar feel, and skin feel after wash can be quantified with instruments (with varying degrees of difficulty) or by trained technicians, but sometimes a human evaluation may be the best way to assess a consumer preference or sensation. Consider fragrance assessment for a bar soap. A gas chromatograph can certainly identify and quantify the mass transport of molecules from the product into the atmosphere, but the assessment of the fragrance's likeability is a qualitative judgment made by a person. Thus, an expert or an untrained consumer panel might be used to help select an appropriate fragrance for a product, and the qualitative judgments of the panelists can be mapped onto a scale to provide a quantitative measure if necessary. In the case of lather, where volume or generation speed can certainly be quantified by an instrument or an expert evaluator, the sensory experience for the consumer remains the characteristic that will influence product acceptance. An instrumental measure may not correlate adequately with consumer preference or may distinguish subtleties that are beyond the average consumer's perception. In such cases, a panel test provides the most relevant product appraisal, and familiarity with some of the basics of consumer testing is useful for the product development scientist.

Moskowitz (1984) has reviewed consumer testing procedures. We note several testing methodologies for use with small panels that could help guide product development at the early stages. Forced-choice tests, such as the triangle test or the same-different test with pairs of prototypes, can be used with relatively small numbers of panelists. Panelists are asked to distinguish the different product in a set of three choices, or they are asked to judge whether a pair of products are the same or different and, if different, to state what the difference is. There are a number of systematic errors to avoid. Expectation error arises when panelists have too much information. This information may include spurious hints, such as when a label (such as 1 or a) is assigned to a prototype that has nothing to do with real properties of the prototype, but it triggers a general bias that people have (for example, paying more attention to objects in a set labeled 1 or a). This type of expectation error can be avoided by assigning random three-digit codes to the prototypes. Another systematic error is positional error. The triads of samples in the triangle test should not be arranged in a line, due to people's bias toward selecting the middle object in this arrangement; instead, the prototypes should be arranged in a triangle, which gives the procedure its name. Also, the arrangement of samples needs to be randomized from panelist to panelist in any test where panelists compare multiple prototypes. Standards have been written to implement various kinds of sensory product tests so that these errors are avoided. (See ASTM E1885-04 concerning the triangle test.)

Bar Hardness

Cleansing bar hardness is not a product trait that generally determines consumer acceptance, since most marketed products show little variation as far as the consumer can assess. All products meet some threshold level of hardness at room temperature, and whatever differences might be revealed by an instrumental test are usually not discernable to the touch. Thus, the basic consumer requirement regarding hardness is that the soap bar not be malleable when it is gripped. However, a bar must be malleable to some degree, so that when a larger stress is imposed quickly, as when the user drops a bar, the product dents rather than shatters. This behavior is ensured by the phase structure of cleansing bars, which we discuss later, and a room-temperature hardness test for a cleansing bar is merely used to reject clearly inadequate formulations during development.

Hardness tests are much more important on the production floor, because the optimum factory production rate and product quality are achieved over a certain range of product hardness. Soap manufactured by extrusion and stamping will have numerous stamping defects if it is too soft, whereas soap that is too hard can lead to unsteady extrusion rates or can reach a limiting extrusion rate that falls below the desired production rate. Soap bars manufactured by casting may also suffer from handling defects if they are too soft, but extrusion and stamping are more sensitive to material hardness, so our summary of assessment methods primarily concerns extruded bars. Different batches of the same nominal formulation may exhibit different hardness on the factory floor due to variation in characteristics of the raw materials, like fatty chain length distribution or moisture, and environmental factors, such as different ambient conditions in the factory or different storage conditions, either of which will result in variation in the moisture level and temperature of the product as it enters the extrusion operation.

The most practical hardness characterization methods for cleansing bars in the factory environment involve indentation or penetration experiments using a needle, cone, or wire. The manufacturers of these devices may refer to the measurement as a hardness test, or a measure of yield stress or consistency. We will define these terms more rigorously in the next section. Consider a penetration experiment, in which a cone is driven into a soap sample by its weight, and the movement of the cone is arrested by the resistance of the soap. Penetration eventually stops when enough of the cone has entered the soap so that the material resistance to deformation balances the load. The penetration depth serves as a measure of product softness. Alternatively stated, a force balance when the cone penetration stops can be used to determine the hardness H, resulting in the following definition:

$$H = \frac{W}{A_c} = \frac{W}{\pi d^2 \tan^2 \alpha} \qquad \text{(Eq. 11.1)}$$

where W is the total load (weight) that causes the deformation, and A_c is the contact area, which is expressed in terms of the depth d and angle α of the cone (see Figure 11.6). This formula allows results of tests with different cones and weights to be compared, though it may be best to fix the cone and weight and simply track the depth of penetration.

The hardness H defined in Equation 11.1 has units of stress, and this may be associated with the yield stress (that is, is the minimum stress required to cause the material to

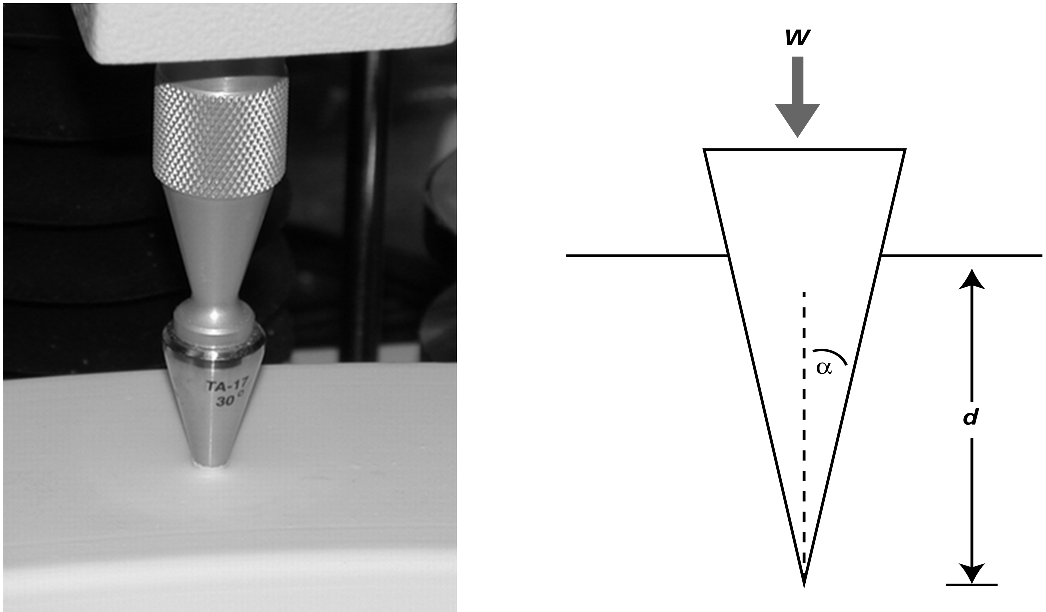

Figure 11.6 Cone penetrometer.

flow), because the cone has, for practical purposes, stopped moving, and the material is resisting deformation at the stress H. Analysis of this test in terms of fundamental material parameters is difficult because two kinds of stress are involved: extensional stress (in the direction of the applied force) and frictional stress (tangent to the cone surface). Separation of these effects requires more detailed knowledge of material properties for a soft solid like soap. A more rigorous discussion of indention tests and their relation to yield stress can be found elsewhere (Adams et al., 1996). Another difficulty with the test is that a soap continues to deform under any load, so the choice of time point when the cone appears to stop is arbitrary. If we wait twice as long, or 10 times longer, the depth of the cone will be greater by some amount—we are merely approaching a zero penetration rate. Thus, implementation of the cone penetrometer test and similar tests requires selection of consistent procedures, including specification of the weight, the geometry of the penetrator, and the contact time. Some standard methods can be used with minor modifications, such as the standard ASTM test for cone penetration of petrolatum, or needle penetration in bituminous materials, or petroleum waxes (ASTM International, 2004–2007).

A less common penetrometer that uses a wire to slice through soap is shown in Figure 11.7. Note how a cross section of soap is positioned in the holder. As in the case of the cone penetrator, the wire comes to rest when it has penetrated enough soap that material resistance balances the weight. For this geometry, hardness is defined by force over projected area:

$$H = \frac{W}{A_c} = \frac{W}{Ld} \qquad \text{(Eq. 11.2)}$$

where L is the length of soap supporting the weight when the wire comes to rest, and d is the wire diameter. Again, a contact time should be arbitrarily selected (a minute is appropriate), because the wire will continue to penetrate the soap, albeit very slowly.

Another type of experiment involves subjecting soap to a constant strain rate (constant rate of probe movement) and measuring the force required to maintain the strain rate. The force or stress associated with a moving probe is sometimes referred to as *consistency*. Barnes (1980) described some of the earliest reported hardness tests on soap by Bowen and Thomas (1935) and by Vold and Lyon (1945). These researchers used sectilometry, that is, the movement of a wire through a material. Barnes repeated the experiments of

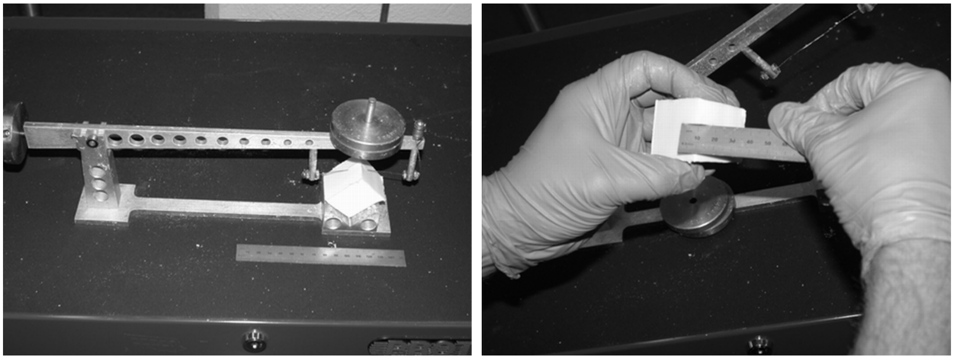

Figure 11.7 Wire penetrometer.

the original studies and cast his results in terms of tensile stress σ versus extensional strain rate $\dot{\varepsilon}$, defined as follows:

$$\sigma = K_1 \frac{F}{2\ell R} \qquad \text{(Eq. 11.3)}$$

$$\dot{\varepsilon} = K_2 \frac{2V}{R} \qquad \text{(Eq. 11.4)}$$

where ℓ is the length of wire moving through the soap, R is the wire radius, V is the velocity of the wire, and K_1 and K_2 are dimensionless constants. He suggested that K_1 and K_2 can both be taken as unity. The original workers reported the force required for a given V, or in the limit as V approached zero. Barnes plotted tensile stress as a function of $\dot{\varepsilon}$ and extrapolated to $\dot{\varepsilon}= 0$, which provides the effective yield stress for extensional flow. He found yield stress to be in the range of $2–5 \times 10^5$ Pa for typical toilet soap.

Instruments are available that perform constant stress or constant strain rate experiments with various probes. A universal penetrometer is a simple device that releases a weighted needle or cone into a material and measures the maximum depth of penetration; the Humboldt Manufacturing Company (2008) offers one example. This is a constant stress experiment, and the device reports a penetration depth, but does not report a hardness such as the one defined by Equation 11.1. ASTM test D5-05a for hardness of bituminous materials, noted in ASTM International, describes how this penetrometer is used. A simple handheld device called a Green Hardness Tester (473 "B" Scale model), made by Dietert for the foundry industry to measure the hardness of green sand molds, would be appropriate to evaluate soap on the production line (Dietert Foundry Testing Equipment, Inc., 2008). This device uses a spring-loaded ball-point-pen-like penetrator and measures the penetration depth. The so-called texture analyzer, marketed by Stable Micro Systems, Ltd. (2008) is a more sophisticated penetrometer, which finds extensive application in the food industry. An operator can choose from a variety of penetration tools. The maximum force is recorded for settings of penetration velocity and maximum penetration depth. The Chatillon mechanical tester, MT 150 series, is another example of a sophisticated penetrometer that provides force as a function of penetration rate (Chatillon Brand Products, 2008).

Rheological Characterization

Rheology is the study of the flow and deformation behavior of materials (Macosko, 1994). Measurement of soap hardness is only one aspect of its rheological behavior. A better understanding of soap behavior during extrusion and stamping operations requires a more complete characterization of soap rheology. A thorough review from 1980 (Barnes, 1980) remains the most comprehensive and relevant discussion of the subject in the open literature. In the years since his review, the rheology of bar soap materials has rarely been presented in peer-reviewed scientific literature, and published work has largely been confined to the patent art.

The material structure of soap at usual extrusion processing temperatures (38–45 °C) on the colloidal length scale (≈0.001–1 micron) is a concentrated suspension of various solids in a viscous fluid, and has been likened to "bricks and mortar" (Hill & Moaddel, 2004). The solid bricks comprise, in large part, C16 and longer-chain saturated fatty soap crystals that are embedded in a continuous mortar phase comprising C12 and shorter saturated soaps, C18 unsaturated soaps, water, and salts. Other solids, such as talc, clays, and starches, may be dispersed in the mortar phase. The bricks, or long-chain fatty soap crystals, represent about 42% by weight, judging from known chain-length distributions for a soap bar composed of only 80/20 tallow/coconut soap at 15% moisture. The mortar is a mixture of solid and liquid whose relative amounts depend on the temperature. We expect only about half of the mortar to be solid in the processing temperature range.

The phase structure of soap controls its rheological properties, which in turn define the limits for extrusion and stamping. Extrusion processing lines are frequently designed to be controlled by the stamping machine. A stamping rate is set, and a control loop will adjust the extruder to deliver soap at the required rate, so the extruder screw speed will adjust accordingly. A soap formula usually increases in temperature as it passes through the extrusion process, which may consist of one or more refiners and a final extruder. The temperature increase of the soap effectively adjusts the ratio of liquid in the mortar phase to allow the soap to extrude at the specified rate. There is a screw speed associated with maximum throughput for a given soap material, above which slower throughput occurs because the soap churns, that is, rotates on the screw. Churning is caused by excessive formation of liquid phase, which reduces friction at the extruder barrel wall. The phase structure and resulting rheology of a soap formula should allow it to extrude at the rate demanded by the stamper, but too large a rise in temperature causes excessive softening, which leads to a high occurrence of stamping defects. Thus, characterization of soap rheology, especially as a function of temperature, provides insight into the processing limits of a formulation.

The term “soft solid” is an appropriate description of soap material. A soft solid is a material that behaves as an elastic solid when subjected to small strains for a short time, deforms and does not recover its original shape when subjected to large strains, and can be made to flow like a fluid when stress exceeds a critical value, which is the yield stress. A concise scientific term for such a material is a *viscoelasto-plastic fluid* (Adams et al., 1996). The relation between stress σ and strain ε for soap has been described by Hooke’s law below the yield stress σ_y,

$$\sigma = E\varepsilon \text{ for } \sigma \leq \sigma_y \qquad \text{(Eq. 11.5)}$$

where E is the elastic modulus, and the relation between stress and strain rate $\dot{\varepsilon}$ above the yield stress is given by the Hershal-Bulkley equation:

$$\sigma = \sigma_y + k\dot{\varepsilon}'' \text{ for } \sigma > \sigma_y \qquad \text{(Eq. 11.6)}$$

where k is called the flow consistency, and n is the flow index. The behavior, as indicated by Equations 11.5 and 11.6, is depicted by the dashed line in Figure 11.8. The determination of yield stress depends on the experimental method used, and the sharp distinction between the regimes governed by Equation 11.5 and Equation 11.6 is an idealization. Barnes has argued that no soft solid has a true yield stress, since nearly all soft-solid materials will flow or deform under a finite stress if we wait long enough (Barnes, 1999). In spite of this observation, Equation 11.6 remains a meaningful description for the flow behavior of soft solids like soap.

Ram extrusion through an orifice can be used to make a practical estimate of the yield stress of soft solids, and to obtain the flow consistency and flow index as well. This

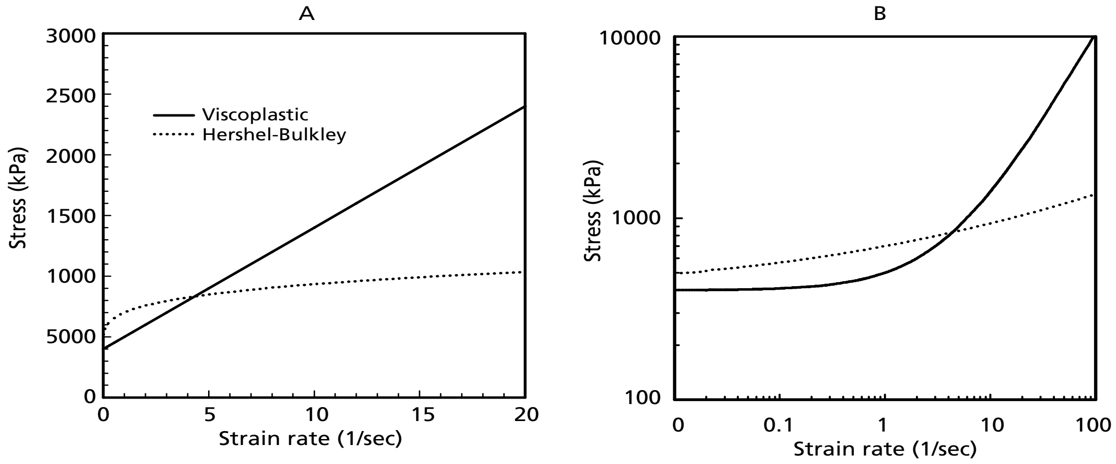

Figure 11.8 Rheological behavior of a soft solid. Viscoplastic and Hershel-Bulkley models depicted on linear scale (a) and log-log scale (b).

experiment can be performed with a capillary rheometer device using an orifice fitting. The soap is forced by a ram of diameter D_r through an orifice of diameter D located at the bottom of a cylinder (cylinder diameter $\cong D_r$), and the force F required to move the ram at speed V_r is recorded by a force transducer. Benbow and Bridgewater (1993) derived a semi-empirical relation, known as the Benbow-Bridgewater equation, for the pressure drop of paste forced through an orifice:

$$P = 2\left(\sigma_y + c\mathrm{V}^n\right)\ln\frac{D_r}{D} \qquad \text{(Eq. 11.7)}$$

where V is the exit velocity of the material and P is the pressure drop. The measured force F on the ram is related to P by $P = \frac{F}{\pi D_r^2}$, and the exit velocity V is related to the ram velocity V_r by $V = V_r(D_r/D)^2$. The σ_y and n of Equation 11.7 are the yield stress and flow index of the Hershel-Bulkley relation, Equation 11.6, and c is a constant. The yield stress is found from experiment by plotting pressure drop versus velocity and determining the intercept of the curve on the pressure axis, which is 2 σ_y ln (D_r/D). If desired, the flow index can be determined as the slope of the asymptote of log(P) versus log(V) for large V.

Basterfield and coworkers (2005) have shown that all three Hershel-Bulkley parameters can be obtained through a more rigorous analysis of orifice extrusion. They obtained an expression for pressure drop similar to the Benbow-Bridgewater equation:

$$P = 2\sigma_y \ln\left(D / D_d\right) + Ak\left(\frac{2V}{D}\right)^n \left(1 - \left(\frac{D}{D_r}\right)^{3n}\right) \qquad \text{(Eq. 11.8)}$$

where the quantities have the same definitions as above, and A is a parameter related to the geometry and the flow index n, which the authors suggest can be approximated as

$$A - \frac{2}{3n}\left[\sin\phi(1 + \cos\phi)\right]^n \qquad \text{(Eq. 11.9)}$$

The $\emptyset$ earlier is an angle associated with the funneling of material as it passes through an orifice. Basterfield and coworkers indicate it can be approximated by 45°. We refer the interested reader to Basterfield et al., 2005 for more detail. Extracting all three Hershel-Bulkley parameters from Equation 11.8 is slightly more complicated than extracting the set of parameters from Equation 11.7, but the yield stress is determined in the same way.

The values of yield stress and the other Hershel-Bulkley parameters depend on temperature and formulation and especially on moisture level. For superfatted toilet soap at room temperature, Barnes (1980) has provided order-of-magnitude estimates of

$$\sigma_y \sim 5 \times 10^5 \text{ Pa}$$
$$k \sim 3 \times 10^5 \text{ Pa}$$
$$n \sim 0.2$$

(Note: The text in this reference indicates a different order of magnitude for the first two parameters, but the figures suggest the values shown here.)

It would be convenient if factory operation could be modified in response to hardness measurements made online automatically or by an operator, but few adjustments on the factory floor can be made to alter product rheology. Addition of small amounts of water to the pellet mixer can be used to soften material, and a soap can be made harder by doing less mechanical work on it. One simple mechanical change can be implemented by replacing a screen in a refiner with one having a larger or smaller mesh size. A larger mesh, or no screen at all, will result in less work done on the soap, and should lower the extrusion temperature, making the soap slightly harder. The disadvantage of this approach is that a screen of a certain mesh size may be required to adequately blend a dye into the soap.

Ideally, a formulation that is too soft or too hard to be manufactured with the factory equipment would be excluded during the product development process, or the equipment would be modified to accommodate the formulation. However, measurement of product hardness in the factory remains a useful exercise to determine how the production line performance correlates with variation in factors like soap composition (within the bounds of a formulation or for different formulations), ambient temperature and humidity, storage history, and mechanical settings.

Conclusion

Manufactured soap bars have existed for centuries, and appraisal methods have evolved together with technological understanding of the product and consideration of consumer needs. This chapter has provided an introduction to current appraisal methods used to evaluate properties of personal wash bars relevant to the consumer, and to the rheology of bar materials relevant to processing. Typically, individual companies describe appraisal methods in internal documentation, which is generally not accessible to the public, so we have attempted to provide the reader with references from the open literature as much as possible, for example, from the patent art and from scientific or engineering publications. Therefore, the chapter may also serve as an entry point for more advanced study.

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12

Glossary

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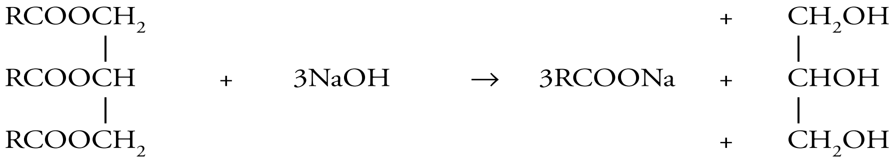
Soap Calculations

Two Routes to Soapmaking

Two primary routes exist for soapmaking:

1. Triglycerides



$$\begin{array}{lllllll} \text{RCOOCH}_2 & & & & & + & \text{CH}_2\text{OH} \\ \quad\ | & & & & & & | \\ \text{RCOOCH} & + & 3\text{NaOH} & \rightarrow & 3\text{RCOONa} & + & \text{CHOH} \\ \quad\ | & & & & & & | \\ \text{RCOOCH}_2 & & & & & + & \text{CH}_2\text{OH} \end{array}$$

Triglyceride + caustic soda → soap + glycerine

2. Fatty acids

$\text{RCOOH} + \text{NaOH} \rightarrow \text{RCOONa} + H_2O$

Fatty acid + caustic soda → soap + water

Fat Blend Calculations

The SV, IV, and titer are all additive of the proportional values of fat blend components. The SV, IV, and titer of an 80/20 blend of tallow (SV 197, IV 45, titer 41) and coconut oil (SV 257, IV 10, titer 22) can be calculated as shown below:

Calculation of SV, IV, and Titer of an 80/20 Tallow/Coconut Oil Blend

Fat Component	(%)	SV	Titer	IV
Tallow	80	197 × 80%	41 × 80%	45 × 80%
Coconut oil	20	257 × 20%	22 × 20%	10 × 20%
Blend	100	209	37.2	38

Caustic Soda Requirement Calculations

The saponification of a fat blend results in the formation of soap and glycerine (Equation 12.1).

$$\text{triglyceride} + 3\ \text{NAOH} \rightarrow 3\ \text{RCOONa} + \text{glycerine} \qquad \text{(Eq. 12.1)}$$

The fat blend and caustic soda are mixed in a nearly stoichiometric ratio, with ~0.1–0.5% excess of alkali. The molecular weight of the fat blend is calculated per Equation 12.2.

$$MW_{fat} = \frac{56.1}{SV} \times 3 \times 100 = \frac{168,300}{SV} \qquad \text{(Eq. 12.2)}$$

Problem 1

Calculate the MW of an 80/20% blend of tallow (SV 197) and coconut oil (SV 258).

$$MW_{tallow} = \frac{168,300}{197} = 854$$

$$MW_{coco} = \frac{168,300}{258} = 652$$

$$MW_{80/20\ T/C} = (854 \times 80\%) + (652 \times 20\%) = 813.6$$

The amount of caustic soda required to saponify a fat blend of known SV can be calculated *via* Equation 12.3.

$$\frac{SV}{1000} \times \frac{MW_{NaOH}}{MW_{KOH}} = \frac{SV}{1000} \times \frac{40}{56.1} = SV \ \times 0.000713_{g/g} \qquad \text{(Eq. 12.3)}$$

Problem 2

Calculate the amount of caustic soda (50%) required to saponify 500 lb of an 80/20% (SV 209) tallow/coconut oil blend.

$$\begin{aligned} NaOH_{50\%} &= SV \times \frac{0.000713}{50} \times 100 \\ &= 209 \times \frac{0.000713}{50} \times 100_{g/g} \\ &= 0.298_{g/g} \times 500 \text{ lb} = 149 \text{ lb} \end{aligned}$$

Saponification Products—Quantity Calculations

The Quantity of Soap

The amount of soap produced in a saponification reaction can be calculated from Equations 12.4, 12.5, and 12.6.

trigylceride + 3 NaOH = 3 soap + glycerine
1 mol + 3 × 40 = 120 = 3 moles + 92

$$Soap_{(wt)} = MW_{fat} + 120 - 92 = MW_{fat} + 28 \qquad \text{(Eq. 12.4)}$$

$$= \left(\frac{fat_{wt}}{fat_{MW}}\right) \times (fat_{MW} + 28) \qquad \text{(Eq. 12.5)}$$

$$= \left(\frac{fat_{wt} \times SV}{168,300}\right) \times \left(\frac{168,300}{SV} + 28\right) \qquad \text{(Eq. 12.6)}$$

The Quantity of Glycerine

Glycerine liberated in a saponification mixture can be calculated from Equation 12.7.

Since triglyceride + 3 KOH = soap + glycerol,

$$\text{glycerine \%} = \frac{\text{SV}}{1000} \times \frac{92}{168.3} \times 100 \qquad \text{(Eq. 12.7)}$$

$$= \text{SV} \times 0.0547$$

$$\text{glycerine}_{\text{wt}} = \frac{\text{SV} \times 0.0547 \times \text{fat}_{\text{wt}}}{100}$$

For fat blends with high levels of FFA, the following calculation will give the glycerine content of the saponification mixtures (Equation 12.8):

$$\text{fat}_{\text{triglyceride}}, (\text{TG}) = \text{SV} - \text{AV} \qquad \text{(Eq. 12.8)}$$

$$\text{glycerine \%} = \frac{\text{TG}}{100} \times \frac{92}{168.3} \times 1000$$

$$\text{glycerine \%} = \text{TG} \times 0.0547$$

Problem 3

Calculate the amounts of soap and glycerine produced in the saponification of a blend of 250 lb of tallow (SV 197) and 250 lb of coconut fatty acid (AV 260; SV 260).

In this case, fat_{wt} = 500 lb, and

	SV	AV
Tallow	197 × 50% = 98.5	
Coconut fatty acid	260 × 50% = 130	260 × 50% = 130

$$\begin{aligned}
\text{TG} &= \text{SV} - \text{AV} \\
&= (\text{SV [tallow]} + \text{SV [coconut fatty acid]}) - \text{AV} \\
&= (98.5 + 130) - 130 \\
&= 228.5 - 130 \\
&= 98.5
\end{aligned}$$

$$\begin{aligned}
\text{glycerine}_{\text{wt}} &= \text{TG} \times 0.0547 \\
&= 98.5 \times 0.0547 \\
&= 5.39\% \\
&= 5.39 \times 500 / 100 \\
&= 26.95 \text{ lb (from Eq. 8)}
\end{aligned}$$

$$\begin{aligned}
\text{soap}_{\text{wt}} &= \left(\frac{500}{168{,}300} \times 228.5\right) \times \left(\frac{168{,}300}{228.5} + 28\right) \\
&= 0.679 \times 76 \\
&= 519 \text{ lb}
\end{aligned}$$

The amount of caustic soda required for this reaction can be calculated per Equation 12.3.

$$\begin{aligned}\text{NaOH}_{\text{wt}} &= 228.5 \times 0.000713 \times 500 \\ &= 81.46\ \text{lb}\ (100\%\ \text{NaOH})\end{aligned}$$

Total Fatty Matter (TFM) Calculation

For product specifications purposes, TFM of a fat mixture is obtained from triglyceride (TG) mass, less its glycerine content, plus water (Equation 12.9).

$$\begin{aligned}\text{triglyceride} + 3\ \text{H}_2\text{O} &= 3\ \text{RCOOH} + \text{glycerine} \\ 3 \times 18 = 54 &= \text{fatty acid} + 92\end{aligned} \qquad \text{(Eq. 12.9)}$$

$$\begin{aligned}\text{TFM} &= (\text{TG} + 54) - 92 \\ &= \text{TG} - 38 \\ \text{TG}_{\text{eq.wt}} &= \frac{56.1}{\text{SV}} \times 1000 \\ \text{FFA}_{\text{eq.wt}} &= \text{TG} - (38/3) \\ &= \left(\frac{56{,}100}{\text{SV}}\right) - 12.66 \\ \text{TFM\%} &= \left(\frac{\text{FFA}_{\text{eq. wt}}}{\text{TG}_{\text{eq. wt}}}\right)\end{aligned}$$

Fatty Acid Blend Calculations

The following three methods are utilized in the calculation of fatty acid and alkali reactants:

1. The molecular weight (MW) method,
2. The gram-mole (G-Mole) method,
3. The acid value (AV) method.

In the molecular weight method, the fatty acid and alkali are blended in the ratio of their molecular weights. The G-Mole method is a variant of the molecular weight method; the reactants are mixed in their grams per mole ratio. The acid value method permits the blending of fatty acids and alkalis on the basis of the acid value of the fatty acid utilized in the neutralization reaction.

$$\text{NaOH}_{\text{wt}} = \text{FA}_{\text{wt}} \times \text{AV} \times 0.713 \times \text{NaOH}\ (\%)$$

Since molecular weight and acid value are interrelated, MW = 56.1/AV × 1000, the molecular weight method will be described in more detail in this chapter.

For fatty acids, the acid value (AV), titer, and saponification value (SV) are all additives of the partial moieties present in the blend. Thus, for a blend of tallow and coconut fatty acids in a 80/20% ratio, the AV of the blend is 218.

Calculation of the Acid Value of a Fatty Acid Blend

Fat Acid Component	(%)	AV
Tallow (AV 205)	80	205 × 80% = 164
Coconut oil (AV 270)	20	270 × 20% = 54
		Total = 218

Caustic Soda Requirement Calculations

For the reaction, $RCOOH + NaOH = RCOONa + H_2O$, use Equation 12.10.

$$FA_{MW} \qquad 40 \qquad (FA_{MW} + 22) \qquad 18 \tag{Eq. 12.10}$$

$$FA_{MW} = \frac{56.1}{AV} \times 1000 = \frac{56{,}100}{AV}$$

$$NaOH_{wt} = \left(\frac{FA_{wt}}{FA_{MW}}\right) \times 40$$

$$= \left(\frac{FA_{wt}}{(56{,}100\,/\,AV)}\right) \times 40$$

$$= \frac{FA_{wt} \times AV \times 40}{56{,}100}$$

Fatty Acid Neutralization Products

The Quantity of Soap Produced

Soap produced in the neutralization reaction can be calculated per Equations 12.11 and 12.12.

$$soap_{wt} = \left(\frac{FA_{wt}}{FA_{wt}}\right) \times \left(FA_{wt} + 22\right) \tag{Eq. 12.11}$$

$$= \left(\frac{FA_{wt}}{FA_{wt}}\right) \times \left(\frac{56{,}100}{AV} - 22\right) \tag{Eq. 12.12}$$

The Amount of Water Produced

This is calculated as per Equation 12.13.

$$water_{wt} = \left(\frac{FA_{wt}}{FA_{MW}}\right) \times 18 \tag{Eq. 12.13}$$

Formula Adjustments

Occasionally, the fatty acid blends or neat soap mixtures require an adjustment of blend composition due to a weighing or calculation error. This section describes practical approaches to handling such manufacturing problems.

Fatty Acid Blend Molecular Weight Adjustment

This adjustment usually requires the addition of a fatty acid of molecular weight lower or higher than the molecular weight of the blend to be adjusted. Equation 12.14 can be used for this purpose.

$$\text{Let } x = \text{portion of fatty acid to be added} \qquad \text{(Eq. 12.14)}$$

$$(1 - x) = \text{portion of fatty acid blend to be adjusted}$$

$$x\,(\text{FA added})_{\text{MW}} + \{(1 - x) \times [\text{FA (initial blend)}_{\text{MW}}]\} = \text{FA(final blend)}_{\text{MW}}$$

Problem 4

You have a tallow/coconut fatty acid blend of MW 244. How much tallow fatty acid (MW 274) should be added to it to convert it into a blend of MW 255?

From Equation 12.14, let x = portion of tallow fatty acid (MW 274) to be added; $(1 - x)$ = portion of initial blend (MW 244).

$$\begin{aligned}
x(274) + [(1 - x)244] &= 255 \\
(274x) + (244 - 244x) &= 255 \\
(274x) - (244x) &= 255 - 244 \\
30x &= 11 \\
x &= 0.37;\ \text{or } 37\% \\
(1 - x) = 100 - 37 &= 63\% \\
\text{Thus, fatty acid blend (initial)} &= \text{MW } 244 \times 63\% = 153.7 \\
\text{tallow fatty acid added} &= \text{MW } 274 \times 37\% = 101.3 \\
\text{final blend} &= \text{MW } 255
\end{aligned}$$

An alternative to this calculation is described in Equation 12.15.

$$\begin{aligned}
\text{Let initial fatty acid weight} &= \text{Wt}_1;\ \text{MW} = \text{MW}_1 \qquad \text{(Eq. 12.15)} \\
\text{final fatty acid weight} &= \text{Wt}_2;\ \text{MW} = \text{MW}_2;\ \text{and} \\
\text{fatty acid added weight} &= x;\ \text{MW} = \text{MW}_3
\end{aligned}$$

$$\text{FA added}_{\text{wt}} = \left(\frac{\text{Wt}_1}{x}\right) - \text{Wt}_1$$

$$x = \frac{\text{MW}_3 - \text{MW}_2}{\text{MW}_3 - \text{MW}_1}$$

Problem 5

You have a 100 lb blend of fatty acid, MW 244. How much of a fatty acid of MW 274 should be added to it to make a final blend of MW 255?

$$x = \frac{274 - 255}{274 - 244} = \frac{19}{30} = 0.633$$

$$\text{FA added}_{\text{wt}}\left(\frac{100}{0.633}\right) - 100 = 58.0 \text{ lb}$$

Thus, FA initial$_{wt}$ = 100 lb (63%) Fa initial$_{MW}$; 244 × 63% = 153.7
FA added$_{wt}$ = 58 lb (37%) Fa added$_{MW}$; 274 × 37% = 101.3
FA final blend$_{wt}$ = 158 lb Fa final blend$_{MW}$; = 255

Alkalinity/Acidity Adjustment

In cases of the downward adjustment of the acidity of superfatted formulas, Equation 12.16 can be used, where FFA refers to the free fatty acid to be neutralized.

$$\text{FFA}_{\text{wt}} = \text{soap}_{\text{wt}} \times \text{FFA}_{\%} \qquad \text{(Eq. 12.16)}$$

$$\text{NaOH}_{\text{added}} = \left(\frac{\text{FFA}_{\text{wt}}}{\text{FFA}_{\text{MW}}}\right) \times 40$$

$$= \left(\frac{\text{FFA}_{\text{wt}}}{\text{FFA}_{\text{MW}}}\right) \times \left(\frac{40}{\text{NaOH}_{\%}}\right) \times 100$$

Problem 6

A neat soap batch (400 lb) was found to contain 3% FFA (MW 280). How much NaOH (50%) should be added to it to make it neutral?

$$\text{FFA}_{\text{wt}} = 400 \times 3\% = 12 \text{ lb}$$

$$\text{NaOH}_{\text{added}} = \left(\frac{12}{280}\right) \times \left(\frac{40}{50} \times 100\right) = 3.4 \text{ lb}$$

The upward adjustment of the FFA level of a neat soap blend is done via Equation 12.17.

$$\text{conversion factor, CF} = \frac{\text{soap}_{\text{wt}} - (\text{soap}_{\text{wt}} \times \text{FFA initial}_{\%})}{\text{soap}_{\text{wt}} - (\text{soap}_{\text{wt}} \times \text{FFA final}_{\%})} \qquad \text{(Eq. 12.17)}$$

$$\text{FFA added}_{\text{wt}} = (\text{CF} \times \text{soap}_{\text{wt}}) - \text{soap}_{\text{wt}}$$

Problem 7

You have a 400 lb batch of neat soap with FFA (MW 280) of 1%. How much FFA (MW 280) should be added to it for a final FFA (MW 280) content of 2% in the neat soap?

$$\text{CF} = \frac{400 - (400 \times 1\%)}{400 - (400 \times 2\%)} = \frac{400 - 4}{400 - 8} = 1.01$$

$$\text{FA added}_{\text{wt}} = (1.01 \times 400) - 400 = 4.0 \text{ lb}$$

The adjustment of a formula of high alkalinity, via the addition of a fatty acid, is performed by Equation 12.18.

$$\text{alkali}_{\text{wt}} = \text{soap}_{\text{wt}} \times \text{alkalinity}_{\%} \qquad \text{\{Eq. 12.18)}$$

$$\text{FA added}_{\text{wt}} = \frac{\text{alkali}_{\text{wt}} \times \text{FA}_{\text{MW}}}{\text{alkali}_{\text{MW}}}$$

Problem 8

A 400 lb batch of neat soap has an alkalinity of 1.6% (as NaOH). How much of a fatty acid of MW 280 should be added to it to make the net soap neutral?

$$\text{alkali}_{\text{wt}} = 400 \times 1.6\% = 6.4 \text{ lb as NaOH}$$

$$\text{FA added}_{\text{wt}} = \frac{6.4 \times 280}{40} = 44.8 \text{ lb}$$

The molecular weight interconversion of fatty acids can be calculated via (Eq. 12.19).

$$\frac{\text{FFA}_A}{\text{FFA}_B} = \frac{\text{MW}_A}{\text{MW}_B} \qquad \text{(Eq. 12.19)}$$

Problem 9

A soap bar sample contains 2% coconut fatty acid (MW 207) as the superfat. Convert this and express it as tallow fatty acid (MW 273) superfat value.

$$\frac{2}{\text{FFA}_B} = \frac{207}{273}$$

$$\text{FFA}_B = \frac{2 \times 273}{207} = 2.63\%$$

Problem 10

A 400 lb batch of soap contains 2% coconut fatty acid (MW 208) as superfat. How much additional coconut fatty acid should be added to this batch to contain a total of 4% superfat, expressed as stearic acid (MW 274)?

In this example, we need to determine the amount of coconut fatty acid present initially in the soap, the above quantity expressed as stearic acid, the additional amount of coconut fatty acid required, and that quantity expressed as stearic acid.

From Equation 12.19,

$$\text{stearic FA}_{\text{initial}} = \frac{208}{274} \times \frac{274 \times 2}{208} = 2.63\%$$

$$\begin{aligned} \text{FFA}_{\text{added}} &= \text{FFA}_{\text{calculated}} - \text{FFA}_{\text{initial}} \\ &= 4.0 - 2.63 \\ &= 1.37\% \end{aligned}$$

The above quantity of stearic acid to be added should then be converted into the coconut fatty acid equivalent, as per Equation 12.19.

$$\frac{\text{FFA}_\text{A}}{\text{FFA}_\text{B}} = \frac{\text{MW}_\text{A}}{\text{MW}_\text{B}}$$

$$\frac{\text{FFA}_\text{A}}{1.37} = \frac{207}{274}$$

$$\text{FFA}_\text{A} = \frac{13.7 \times 208}{274} = 1.04\% = (400 \times 1.04\%) = 4.16 \text{ lb}$$

The batch contains now a total of 8.0 + 4.16 = 12.16 lb (3.01%) of coconut fatty acid. This is equivalent to 4% stearic acid, as per Equation 12.19.

The calculation for the adjustment of alkalinity follows:

- The alkalinity of a formula containing FFA can be increased as per Equation 12.20.
- First, calculate the amount of alkali needed to bring the formula to neutrality via Equation 12.16. Then, the amount of additional alkali needed to reach the desired alkali level is calculated.

$$\text{alkalinity adjustment, AA} = \frac{\text{alkali final}_{\%}}{100} - \frac{\text{alkali initial}_{\%}}{100}$$

$$\text{alkali}_\text{wt} = \frac{\text{AA} \times \text{soap}_\text{wt}}{\text{alkali}_{\%}}$$

Problem 11

For a 400 lb batch of neat soap containing 2% FFA (MW 270), how much NaOH should be added to increase the alkalinity (as NaOH) to 0.1?

$$\text{From Equation 16, } \text{FFA}_\text{wt} = 400 \times 2\% = 8 \text{ lb} \qquad \text{(Eq. 12.20)}$$

$$\text{NaOH added} = \frac{8}{270} \times 40 = 1.18 \text{ lb}$$

$$\text{From Equation 20, } \text{AA} = \frac{0.1}{100} - \frac{0}{100} = 0.001$$

$$\text{NaOH}_\text{wt} = \frac{0.001 \times 400}{100} \times 100 = 0.4 \text{ lb}$$

$$\text{NaOH total added} = 1.18 + 0.4 \text{ lb} = 1.58 \text{ lb} \times 100$$

The alkalinity of a formula, which is already alkaline, can be increased further by Equation 12.20; the alkalinity of a formula can be decreased by the addition of a fatty acid via Equation 12.18.

Problem 12

A 400 lb batch of neat soap contains 2% FFA (MW 270). How much of a 30% NaOH solution should be added to it to bring the FFA level to 1% (MW 208)?

A combination of equations will be used for this calculation.

$$\text{FFA}_{\text{wt}} = 400 \times 2\% = 8 \text{ lb}$$

From Equation 12.19,

$$\frac{8}{\text{FFA}_\text{B}} = \frac{270}{208}$$

$$\text{FFA}_\text{B} = \frac{8 \times 208}{270} = 6.16 \text{ lb}$$

Now, the batch requires 400 × 1% = 4 lb FFA (MW 208). Thus, excess FFA (MW 208) = 6.16 – 4 = 2.16 lb. To neutralize 2.16 lb of fatty acid with 30% NaOH, Equation 12.12 is utilized:

$$30\% \text{ NaOH added} = \frac{2.16}{208} \times \frac{40}{30} \times 1.38 \text{ lb}$$

To summarize in molar equivalents, the formulas containing free fatty acids will have the following weight ratios:

$$\text{coconut fatty acid}_{\text{wt}} < \text{stearic acid}_{\text{wt}}$$

To illustrate, 5% coconut fatty acid, MW 208 (as FFA) = 6.6% stearic acid, MW 274 (as FFA). Therefore, it will take a greater quantity of stearic acid than coconut fatty acid to neutralize a given quantity of alkali.

Terminology/Definitions

Acid Value (AV)

The Acid Value is the number of milligrams of potassium hydroxide (KOH) necessary to neutralize the fatty acids in 1 gram of sample.

$$\text{RCOOH} + \text{KOH} \rightarrow \text{RCOOK} + \text{H}_2\text{O}$$

- Higher AV materials allow faster appearing but less stable suds creation.
- Lower AV materials allow slower to appear but more stable suds formation.
- Lower acid value means more cleansing (detergency).
- AV is used only on fatty acids to provide an estimate of SV. The AV for fatty acids is very close to the SV. AV usually runs about 2 points lower than the SV.

Commercially-Used Color Scales

APHA

For light colored liquids; compares light absorption relative to Pt-Co standards.

Gardner

Measures in step; compares sample color to standards of specified colors with associated "Gardner numbers."

Lovibond Color

Color measurement of the fats, oils, and fatty acids determined with a Lovibond Tintometer. A 5¼-inch glass cell containing the sample is compared with Lovibond glass red (R) and yellow (Y) color standards and the colors are recorded in R and Y units. The R value is the color controlling value. The results are cell dependent.

- R value of 1.0 or less is preferred for the production of white soaps.
- R value above 2.5 will result in less off white (darker color) soaps.

Spectrophotometric

Continuous scale; measures transmission percentage at 440 nm and 550 nm.

Fatty Acids

Fatty acids are linear, mostly even carbon-numbered long-chain hydrocarbons with a terminal carboxyl group. Unsaturated fatty acids are those with one or more double bonds in their carbon chain structure.

Notes on Fatty Acid Profiles

- Long chain C_{14} to C_{20} fatty acids provide best cleaning but minimal sudsing.
- Short chain C_6 to C_{12} fatty acids provide faster but less stable suds and lower cleansing than long chain fatty acids.
- C_{12} provides best sudsing.
- C_{18} provides best cleaning. Among long chain fatty acids, unsaturated fatty acids provide better cleansing.
- Saturated fatty acids are more stable to oxidation, discoloration, and rancidity.
- Extra-long-chain fatty acids (C_{22} and higher) do not contribute much to either sudsing or cleansing but do contribute to bar integrity.
- High sudsing does not mean high cleansing. However most consumers do not think that way.

Mixing Oils and Fatty Acids for Soap Making

- Mixtures of high and low SV stocks provide a very desirable lever of foaming and cleansing.
- Typically, 10–30% of high SV and 70–90% of low SV triglyceride oils are used.
- The average AV or SV is calculated, based on the percentage weight ratio of fatty acids or oils. The amount of sodium hydroxide used is based on this average value.
- High foaming does not mean high cleansing, however, most consumers think that way.
- Examples of high SV oil: coconut, palm kernel, babaçu.
- Examples of low SV oils: tallow, palm, canola (rapeseed), rice bran.
- For detailed analytical testing procedures, please consult the official AOCS Methods.

Free Glycerine

The amount of free glycerine present in the sample expressed as percentage weight of the total sample.

- Perceived as a moisturizer.
- The foam volume (mL) is determined using a 0.1% soap solution.

- Glycerine up to 2% give softer and stickier soap.
- Glycerine levels above 2% will harden the soap.
- Used as a processing aid for low moisture, high titer products.

Free Alkalinity (Free Caustic)

Free alkalinity is the amount of alkali content present in a sample expressed as percentage weight of free sodium hydroxide (NaOH).

- The higher free alkalinity, the greater the skin irritation from soap.
- The higher the alkalinity, the greater the cleaning power of soap.
- For toilet soaps, lower alkalinity is preferred for a better product stability with respect to color and odor.
- For laundry soaps, higher alkalinity provides better cleansing properties.

Free Fatty Acid (FFA)

It is the free fatty acid content present in a sample. It is commonly expressed as oleic acid but it can also be expressed as palmitic acid or stearic acid.

Foam Volume

It is the measure of the foamability of a cleansing product.

The foam volume (mL) is determined using a 0.1% soap solution placed in a measuring cylinder and agitated with a perforated paddle stirrer for 30 strokes. The initial measurement was made after agitating the solution and final after 5 minutes standing.

There are different foam test protocol methods. The Ross-Miles method is the most widely used. All the methods give relative volumes and are used for lather comparison. There is no standard method giving absolute values. For more details, refer to Chapter 11.

Iodine Value (IV)

The iodine value is a measure of the unsaturation (double bonds) in fats, oils, and fatty acids. IV is expressed in terms of the number of grams of iodine absorbed by 100 grams of sample (% iodine absorbed).

$$-\mathrm{CH}=\mathrm{CH}- + \mathrm{I}_2 \rightarrow -\mathrm{CHI}-\mathrm{CHI}-$$

The higher the IV, the higher the degree of unsaturation and the greater the vulnerability for rancidity. As the IV level increases, soaps become softer and stickier.

The foam and cleansing increase as the IV increases and decrease as the IV decreases in higher chain saturated fatty acids.

Coconut oil (7–12 IV range) is an exception. It produces the hardest soap, the fastest sudsing, but it lacks suds stability.

The analytical determination is actually carried out using Wijs solution (ICl in acetic anhydride) as opposed to iodine per se.

Melting Point

The temperature expressed in °C at which a triglyceride or fatty acid liquefies.

Moisture Content

It is the amount of volatile materials present in a sample expressed in percentage weight.

Penetration Value

Is a measure of bar soap hardness. It is expressed as the distance (depth) in millimeters a penetrometer needle penetrates a bar of soap when subjected to a 50 gram weight. The deeper the needle travels, the softer is the soap.

Saponification Value (SV)

The saponification value is defined as the number of milligrams of potassium hydroxide (KOH) required to saponify 1 gram of sample.

SV is used to determine the average molecular weight (MW) of fats and oils being saponified, using the formula: $MW = 56{,}100 / SV$.

Mixtures of high and low SV stocks provide very desirable levels of sudsing and cleansing. Typically, 10–30% of high SV and 70–90% of low SV triglycerides are used.

Sodium Chloride

The amount of sodium chloride (NaCl) present in a sample expressed in percentage weight of sodium chloride or simply chloride. Sodium chloride is one of the most critical ingredients for soap processing and product attributes.

Sodium chloride hardens the soap but high levels can create "cracking" and decrease sudsing. In standard nonsuperfatted low coconut content the level should not exceed 0.5%.

The chloride level increases in nonsuperfatted soaps depending upon the level of coco/palm kernel soap in the product. It can be as high as 2–3% in high coconut content containing soaps.

Superfatted soaps can have up to 1.5% sodium chloride without detrimental effects.

Titer

It is the measure of the solidification point of fatty matter (fats, oils, and fatty acids) measured in °C. A peaked or plateau temperature point in the temperature curve profile characterizing the temperature rise in a crystallizing sample due to the release of heat of crystallization.

- Higher titer provides harder soap.
- Lower titer provides better cleansing (with longer chain fatty acids or triglycerides).

Total Fatty Matter (TFM)

Total fatty matter is expressed as the fatty acids obtained from soap. and is the sum of the free fatty acid, the fatty acid obtained from soap and the unsaponifiables. The test method used for determination of TFM requires splitting of soap by using mineral acids and then the extraction of the fatty matter by using petroleum ether. Total fatty matter does not include the fatty matter generated by nonsoapy synthetic actives.

- The TFM of triglyceride is the amount of fatty acids produced by splitting the oil.
- The TFM of fatty acids is the total weight of fatty acids. Fatty acids are 100% TFM.

Unsaponified and Unsaponifiable Matter (U&U)

The unsaponified matter consists of neutral unreacted fat, which is not saponified. The unsaponifiable matter includes substances frequently found dissolved in fats and oils that cannot be saponified with caustic alkalies but are soluble in ordinary fat solvents. U&U is the amount of substances soluble in petroleum ether present in the sample and is expressed in percentage weight.

- High unsaponifiable content makes soap sticky and can lead to discoloration.
- Unsaponifiables contribute to the emolliency and skin feel attributes of soap bars. They basically act as "superfatting" agents and are a part of the TFM.

Selected AOCS Official Test Methods

Test/AOCS Method for:	Fats and Oils	Fatty Acids
Acid value	Cd 3d-63	Te 1a-64
Free fatty acid	Ca 5a-40	—
Insoluble impurities	Ca 3a-46	—
Iodine value	Cd 1d-92	Tg 1a-64
Moisture/volatiles, 130 °C	Ca 2c-25	—
Colorimetric color, Wesson method	Cc 13b-45	—
Colorimetric color, Lovibond method	Cc 13e-92	—
Photometric color	Cc 13c-50	Td 2a-64
Alcoholic saponification color	Cc 13g-94*	—
Refined and bleached color	Cc 8d-55	—
R&B; alcoholic saponification color	Cc 13f-94*	—
Saponification value	Cd 3-25	—
Titer	Cc 14-59	Tr 1a-64
Unsaponifiable matter	Ca 6a-40	Tk 1a-64
Water, Karl Fischer method	Ca 2e-84	Tb 2-64

Test/AOCS Method for:	Soap	Soap with Detergent
Acid value	Da 14-48	—
Anhydrous soap content	Da 8-48	Db 6-48
Chlorides	Da 9-48	Db 7-48
Free fatty acid/free alkali	Da 4a-48	Db 3-48
Glycerin	Da 23-56	—
Iodine value	Da 15-48	—
Moisture and volatiles	Da 2a-48	Db 1-48
Saponification value	Da 16-48	Db 8-48
Titer	Da 13-48	—

*AOCS Recommended Practice

Index

Soap Manufacturing Technology

Second Edition

Edited by Luis Spitz, Highland Park, IL, USA

Soap Manufacturing Technology, Second Edition, is the most authoritative and up-to-date book on soap technology available today. Editor and contributing author Luis Spitz leads a world-renowned team in providing comprehensive information on all components of soap manufacturing including formulation, soap structure and phase behavior, performance evaluation, cleansing systems, finishing systems, and more. This new edition includes two new chapters, “Semi-Boiled and Integrated Saponification and Drying Systems” and “Soap, Soap/Synthetic, and Synthetic Laundry Bars” as well as being fully revised and updated throughout, including new figures, tables and text.

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