

Soap Manufacturing Technology

Second Edition

Edited by Luis Spitz



Soap Manufacturing Technology

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

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1

Implications of Soap Structure for Formulation and User Properties

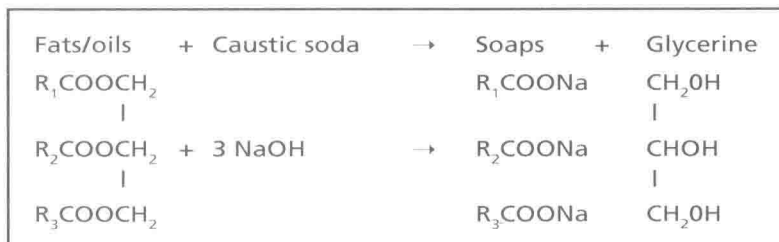
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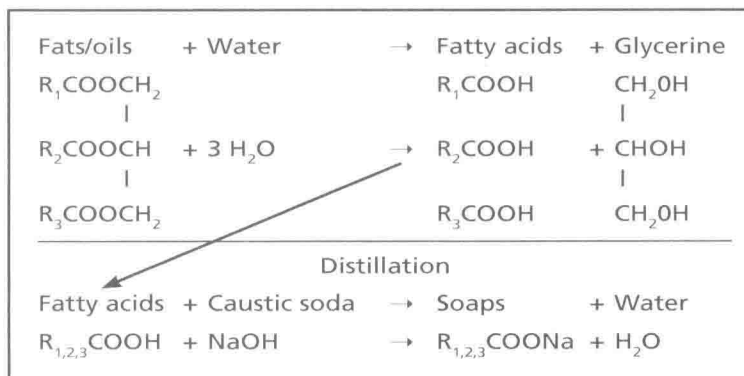
Basic Chemistry

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.



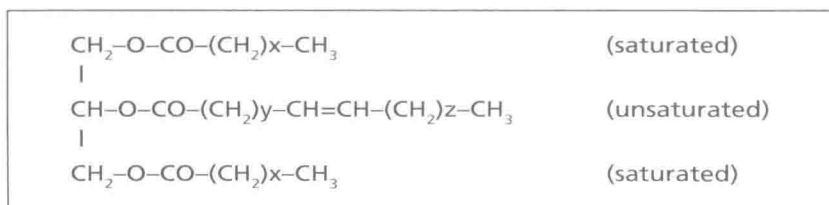
The alternative is to split the triglyceride oil into fatty acids and glycerine using high temperatures and high pressures. In this case the fatty acids and glycerine can easily be separated. The separated fatty acids are normally distilled, blended, and then neutralized with NaOH solution to form soap.



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:



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 tallow (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).

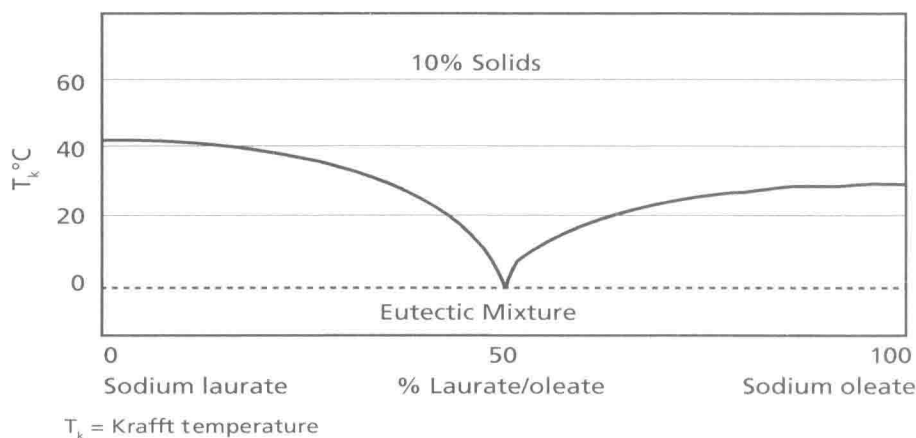


Figure 1.1 Solubility of the Eutectic Mixture from C12 and C18:1 Soaps.

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/m² to 3.8×10^5 N/m². 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 (superfating). 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 mashing.

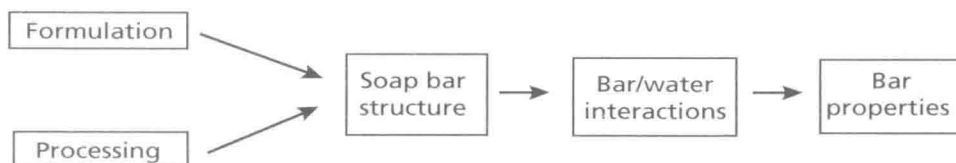
Soap/Water Interactions

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 mashing, and shrinks when the mush dries.
- The amount of mush, and therefore the resultant stress, are influenced by both formulation and processing.