SOAP

1. Introduction

Soap is one of the oldest known manufactured chemical substances and was first produced over two thousand years ago through the reaction of animal fats with the ashes from plants (1–2). Initially soaps were used primarily for the cleansing of clothing. The earliest documentation of their use as a medicament and for personal hygiene did not appear until the beginning of the second century. Details of the subsequent development of soap-making are rare but by the Middle Ages soap-making was prevalent across Europe. By this time soap-making had moved on from a cottage industry into an industrial process. Two types of soap were available depending on location. Coastal producers used ash from sea weeds which was rich in sodium carbonate, and hence made hard soap directly. In contrast, central European makers used wood ash which was rich in potassium carbonate, and produced soft soaps or used salt to convert this into hard soap. This situation prevailed until the late eighteenth century when Leblanc developed a low cost process for the manufacture of soda ash which removed the restriction of cost on hard soap production.

By the late nineteenth century the basic chemistry of soap making was understood and the principles of kettle soap-making were essentially in place. The next major developments had to wait until the early twentieth century when physical chemists studied the detailed phase behavior of soap and in parallel Wigner identified a quantitative approach to soap making (3). In combination these activities paved the way for continuous soap making operations using a wide range of oils/fats.

Current mass market soap manufacturing is based primarily around continuous soap making using either fat saponification or by fatty acid neutralization, utilizing a wide variety of natural and synthetic feedstocks. The soap chips produced are then usually finished using a high speed soap line comprised of refiner mill, extruder, and stamper. Batch processing is much rarer and is mainly confined to speciality soaps which often sell at a considerable premium. Examples of such products are high transparency cast bar products.

The strict definition of the term “soap” includes all compounds formed by interaction of either an inorganic or organic base with an organic fatty acid. This general description hence covers chemicals with a wide range of physical properties spanning water soluble to water insoluble. For instance the use of heavy metals or alkaline earth metals produces water insoluble soaps, many of which have industrial uses. However the most important sub-group of soaps are those that display surface activity (such molecules are known as “surfactants” from the description surface active). These soaps are usually based on combinations of alkali metals such as sodium and potassium and linear alkyl chain carboxylates. These simple metal alkyl carboxylates represent the oldest surfactants known. The term surfactant describes molecules which are comprized of two separate groups, one which is water-loving and the other which is water-hating. This combination of properties is responsible for classical surfactant behavior such as interfacial adsorption, lather and emulsion stabilization, detergency and surface wetting. All of these phenomena are due to the balance of hydrophilic/hydrophobic characteristics operating in surfactant molecules.

In the twentieth century, many new synthetic surfactants were developed. These can be manufactured from either the traditional oils and fats used for soap making or from petrochemicals. These surfactants may have advantages over soap, including mildness to skin, high water solubility and most importantly they may not be precipitated by calcium and magnesium ions. The first two of these have led to the growth of liquid products such as shampoos, shower gels and body washes where the use of soap can lead to precipitation at low ambient temperatures. The precipitation of soap by calcium and magnesium ions is a major issue for soap since these ions are present to some degree in all surface waters. The common term for these ions is water hardness. Thus in hard water which contains significant amounts of both calcium and magnesium ions, soap is precipitated as scum. This reduces cleaning efficiency and also lays down an insoluble layer of these precipitates on solid surfaces known as lime-scale. This problem has led to full or partial replacement of soap by new synthetic surfactants in formulations for use in hard water conditions in personal washing, and particularly in laundry washing where build-up of the precipitated soaps will change both fabric appearance and feel over time. In contrast in the bar form products, the move to synthetics has been minimal due to the immense difficulty in incorporating high levels of synthetic surfactants which are either liquids or have paste-like rheology in their anhydrous state.

2. Properties and Phase Behavior

2.1. Physical Properties. A surfactant is a bipolar surface active molecule composed of hydrophilic and hydrophobic groups. For soap molecules, the carboxylate head group, negatively charged, is hydrophilic and interacts with water. The long hydrocarbon chain is hydrophobic and therefore prefers air or an oil phase. Large polymeric surfactants can have more than two hydrophilic blocks separated by a hydrophobic block or another way around.

There are generally four types of surfactants. They are anionic, cationic, zwitterionic, and non-ionic based on the type of charges that the surfactant molecules possess in a solvent, usually water (4,5). Anionics are negatively charged; cationics positively charged; non-ionics are not charged; and zwitterionics possess both negative and positive charges in different parts of the molecule but overall the molecule is neutral. In practice mixed surfactants are often used in commercial formulations. For example in shampoo and shower gels an anionic and a zwitterionic are mixed to enhance the micelle and foam stability. It is, however, not usual to mix anionic and cationic surfactants together since the molecules couple together due to the charge interaction and precipitate.

Surfactants can be crystalline or liquids and dissolve preferentially in water or an oil phase depending on the balance of hydrophobic and hydrophilicity characteristics within the surfactant (4,5). In solution, a range of aggregates may form together with the solvent depending on the surfactant concentration and the temperature. A monolayer of the surfactant molecules normally forms between any two phases of dissimilar polarity, eg, water and oil, or water and air. The hydrophilic portion preferentially solubilizes in the polar or higher polarity phase whereas the hydrophobic portion preferentially solubilizes in the nonpolar or lower polarity phase. The presence of surfactants at the interface provides stability to the interface by lowering the total free energy associated with maintaining the boundary. Thus, surfactants facilitate stabilization of intermixed, normally immiscible phases, such as oil in water, by decreasing the free energy necessary to maintain the large interfacial region associated with mixing. For example, in the absence of surfactants, oil in water dispersions rapidly separate into two distinct layers to minimize the surface or contact area between the two phases. The ability of surfactants to lower this interfacial energy between the oil and water allows the formation and stabilization of smaller oil droplets dispersed throughout the water, forming stable dispersions called emulsions.

Another property of surfactants is their ability to aggregate in solution to form various composite structures or phase states, such as micelles and liquid crystals, as a function of concentration and temperature. At very low surfactant levels, the surfactants exist as individual molecules in solution associating primarily with water molecules. They also concentrate or partition to form a monolayer at the interfacial regions as described above. However, as the concentration of surfactant in solution is increased, a point is reached where the molecules aggregate to form micelles. This concentration is defined as the critical micelle concentration (CMC). The micellar structure minimizes system free energy through surfactant self-association; the micelle in water is typically characterized with the hydrophobic tails pointing to the centre and the hydrophilic head groups pointing out toward the water in spherical superstructures. As the concentration of surfactant in solution is further increased, the micelles elongate into long tubules which align with each other to form a hexagonal arrangement when viewed end-on. These structures are commonly referred to as hexagonal liquid crystals. As the surfactant concentration is further increased, the tubules expand in a second direction to form large, stacked lamellar sheets of surfactants, commonly referred to as lamellar liquid crystals. These liquid crystals are very important in soap making and the washing properties of the soap. In a soap bar, the soap concentration is very high and liquid crystals exist in the soap bar. During washing as the water concentration increases the soap crystal concentration decreases therefore the soap molecules form micelles or individual molecules which stabilize the water and air interface and lead to the formation of foam or lather. In the rinsing stage the soap concentration decreases significantly which causes the collapse of foam.

2.2. Phase Behavior. Soap as an anionic surfactant in water can form a range of aggregates with different shapes and sizes depending on its concentration and the temperature. Its interaction with water is also influenced by the hydrocarbon chain length, the saturation of the hydrocarbon chain and the counter ions property. Furthermore the presence of other surfactants and electrolytes can also significantly change its phase behavior.

Binary Soap–Water System. Mixtures of soap in water exhibit a rich variety of phase structures (4,5). Phase diagrams chart the phase structures, or simply phases, as a function of temperature (on the y-axis) and concentration (on the x-axis). Figure 1 shows a typical soap–water binary phase diagram, in this case for sodium palmitate–water. Sodium palmitate is a fully saturated, 16-carbon chain-length soap. At lower temperatures, soap crystals coexist with a dilute isotropic soap solution. Upon heating, the solubility of soap increases in water. As the temperature is increased the soap becomes soluble enough to form micelles; this point is named the “Krafft point”. The temperature boundary at different soap concentrations above which micelles or liquid crystalline phases form is named the “Krafft boundary” (5).

At typical soap processing temperatures (80–95°C), three liquid soap phases are possible: isotropic (nigre), middle (hexagonal), and neat soap (lamellar) (5). Micelles are observed in dilute soap solutions and are characterized as very fluid. Middle soap is a liquid crystalline phase that is extremely viscous and difficult to handle and work. In commercial soap-making processes, care must be taken to avoid the middle-phase region on account of the physical problems associated with it; neat phase is always approached from the more concentrated soap direction. Neat soap is considerably more fluid than middle phase and is readily pumped and mixed. This is the phase most commonly desired for soap-making. Neat soap is generally found in the concentration range of 60–90% soap, with commercial processes typically targeting ~70% soap as the optimal concentration. Higher soap concentrations require increased temperatures to maintain the fully liquid crystalline properties (note the curved boundary in Fig. 1) and exhibit increased viscosities which become difficult to manage.

With the decreasing of the hydrocarbon chain length the Krafft point and Krafft boundary move towards lower temperatures since the solubility of the soap increases with decreasing the hydrocarbon chain length while the basic features of the phase behavior remains more or less the same. The unsaturation of the hydrocarbon chain also impacts in a similar way as caused by the decreasing of hydrocarbon chain length (4,5).

The counter ion’s impact on the phase behavior is very significant and has been studied extensively for metal ions such as sodium and potassium. Generally speaking, potassium soap is more soluble than the corresponding sodium soap. There are few studies on the amine counter ions such as triethanolamine although amine soap is used widely in making transparent soap and skin care formulations. The studies carried out by Warnheim and Jonsson showed that amine soaps are not only more soluble than the alkaline soaps in water but their phase behavior is much simpler compared with the alkali soaps. For example, triethanolamine palmitate in water forms a lamellar liquid crystal phase at 20°C and no hexagonal liquid crystal phase (6,7). Research work carried out by scientists from Unilever Plc discovered very recently that significant hydrolysis takes place at room temperature for triethanolamine stearate in a 20% aqueous solution. Stearic acid crystals are formed as a consequence of the hydrolysis (8). It is believed that the large size of the counter ions weakens the interactions between the hydrocarbon layers and contributes to the increasing of the solubility.

Ternary Systems. A variety of components such as salt (5), fatty acid (9), and glycerol (10) can be deployed to alter the general phase characteristics of the soap–water system. Ternary phase diagrams are constructed to account for the presence of a third material. These diagrams are displayed as triangles where each of the vertices defines one of the three components and each of the three sides defines the relative concentrations of the two components contained by the two vertices associated with the side. Although temperature continues to be another important variable, these ternary diagrams are often drawn for a defined temperature because of the difficulties in representing an additional dimension. Sometimes the ternary triangle is modified by increasing the angle of one of the vertices to 90°, emphasizing the most important components.

The soap–water–salt diagram is typically shown graphically with the 90° vertices (Fig. 2). At 0% salt, the phases along the axis present a slice of the binary soap–water-phase diagram at 90°C (sodium palmitate in this case). The addition of salt to the system greatly reduces the concentration ranges for the liquid crystalline phases and increases the ranges for the isotropic phases: nigre and lye (a caustic rich aqueous phase). Further increase in the salt concentration drives the system into a biphasic region in which both a concentrated soap and a nigre (or lye) phase coexist. This ability of salt to drive the system into a biphasic, neat soap–nigre/lye phase structure is the basis for the direct saponification approach to soap making. The soap can be separated at a controlled concentration from an aqueous lye or salt phase. The aqueous phase can be used to wash out the excess lye, impurities, and most importantly the glycerol, a valuable by-product of soap-making.

The addition of soluble electrolytes in the soap bar is widely use to increase the bar hardness with the same amount of soap concentration by taking the advantages of the electrolytes effect on the phase changes of soap and water.

In soap bar processing free fatty acid is usually added in formulations to create so-called super-fatted soap. An acid-soap complex with a fixed stoichiometric ratio between alkaline soap and the fatty acid is formed. For example, the ratio of potassium acid soap is 1:1 while sodium soap forms acid soaps with various ratios. The fixed ratio complex exits not only in anhydrous crystalline phase but also in a hydrous liquid crystalline phase (11,12). Oleic acid and its potassium soap form a 1:1 complex acid soap when equal molar acid and soap are mixed. Above the Krafft boundary, the acid soap in water forms a lamellar liquid crystal phase at low surfactant concentration, from a few percent, and the lamellar liquid crystal phase extends to ca 60% surfactant concentration. A hexagonal liquid crystal phase is formed after the lamellar liquid crystal phase with further increasing the surfactant concentration. This phase behavior is different from the soap and water phase behavior, in which the hexagonal liquid crystalline phase is formed first followed by the lamellar liquid crystalline phase. Below the Krafft boundary the acid soap complex forms a solid crystal and separates from water (4).

An acid soap of 2:1 complex ratio was discovered recently between triethanolamine stearate and stearic acid (13). In water the acid soap forms a lamellar liquid crystal phase at high temperatures, above 60°C, and transforms to a lamellar gel phase on cooling. The gel phase, however, is not stable at ambient temperature due to the occurrence of the hydrolysis reaction which converts the soap back to stearic acid which precipitates in the triethanolamine aqueous solution. A polymorphism of C, E and possibly A forms of stearic acid crystals were found resulting from the hydrolysis reaction (8).

2.3. Solid Phases and In-use Properties. *Anhydrous Soap.* The physical properties of anhydrous soaps are varied. The hydrocarbon chains crystallize and form a solid at ambient temperature. A bilayer structure is normally formed from alkaline soap with the hydrocarbon chains orienting perpendicular or tilted to the basal plane. In the bilayer structure the molecules arrange head-to-head and tail-to-tail format (14). On heating the alkaline soap goes through a number of phases, such as curd, subwaxy, waxy, superwaxy, subneat, neat and forms an isotropic liquid at a temperature range of around 200 to 300°C. The exact thermotropic behavior depends on chain length, chain unsaturation and the counterion involved.

The alkaline soaps of various chain lengths, C_{12} to C_{18}, have been studied extensively over the last hundred years. For anhydrous potassium soaps at least three anhydrous forms-A, B, and C-exist (4). Form A is found for soaps containing 4–12 carbon atoms; the B form is obtained for the higher homologues containing 12–18 carbon atoms. Both A and B forms transform to the C form at higher temperatures.

A new soap structure has been recently discovered when triethanolamine is used to neutralize stearic acid. The soap molecules arrange in a tail-to-head format and the chain is perpendicular to the basal plane (15). The melting behavior of the soap is also simpler than the alkaline soaps. Only one transit phase, the lamellar liquid crystal, is observed and the soap melts completely at 93°C (13).

Soap with Low Water Content. For soap with small amount of water, up to 30% water, a total of five crystalline phases, ie, kappa, delta, zeta, eta and gamma have been identified by X-ray diffraction. It should be noted that these descriptions are based on Burger's definition (16) and that the equivalent solid phases also have different nomenclatures in the literature (17). The first four of these phases are produced by cooling specific soaps from aqueous solution while the last, gamma, is only obtained on cooling from aqueous ethanol solution. In a strict sense, these crystalline sodium soap phases are not polymorphs, ie, different crystal arrangement of same composition; rather, they are different phase compounds, ie, compositionally different. This distinction arises not only because of the differences in crystal arrangement but also because of the different levels of hydration present in the various crystalline states as well as the hydrocarbon chain structures, eg, the chain length and unsaturation of the hydrocarbon chain.

It is possible to attach a molecular picture to the soap phases normally encountered in commercial formulations. Therefore, the soap constituents are divided into unsaturated (oleic) and saturated carbon chain-type components, the latter being further subdivided into short chain type components (lauric and myristic chains) and components of the long chain type (palmitic and stearic chains).

Eta phase sodium soaps were found to be connected with the presence of unsaturated carbon chains. This phase was found for pure sodium oleate and in mixtures of this soap and short saturated chain material. Kappa phase corresponds with short chain sodium soaps. It was found for pure saturated sodium soaps of the short chain type and also for mixtures of these and saturated long and short chain-type soaps. Delta phase was found for mixtures of saturated long chain sodium soaps whereas zeta phase only appeared for the pure soaps of this type.

Mixed Soap Crystals in Non-super Fatted Formulation. Soap bars consist of mixture of soaps with different chain lengths and chain saturations. They are classified as soluble soaps and insoluble soaps. The soluble soaps usually form a hexaganol liquid crystalline phase with water, as shown in Figure 1, which dissolves in water during washing and provides lather. The insoluble soaps stay in crystalline formats in the bar and provide mechanical strength. The solid crystals present in a soap bar can include kappa, zeta, eta and delta phases.

The amount of the soluble and insoluble phase in the soap bar is strongly dependent on the water content and the amount of shear/working the soap bar has been subjected to at temperatures above or below the Krafft point of the soap molecules. Increasing water content results in an increase in the amount of soluble soap and consequently a reduction in soap hardness. Processing at temperatures below the Krafft point favors the separation of soluble and insoluble soaps. The separation is achieved by dissolution of soluble soap in the liquid phase and by the creation of a metastable, soluble eta solid. Processing at temperatures in excess of the Krafft point favors recombination of soluble and insoluble soaps into a new, disordered metastable kappa phase solid upon cooling.

Addition of small quantities of electrolyte and perfume can also influence the liquid and solid phase ratio. Electrolyte reduces the soap solubility and therefore increasing the solid phase amount while perfume increases the soluble soap amount.

Mixed Soap Crystals in Super Fatted Formulations. A small quantity of fatty acid, usually less than 10%, is added to normal soap to produce a superfatted soap. The fatty acid is added to the soap phase at temperatures above the fatty acid melting point and new solid crystalline and liquid crystalline phases are formed on cooling.

A fixed stoichiometric ratio complex of fatty acid and soap can form when fatty acid and soap molecules are mixed. In super fatted systems the liquid crystalline phase is a lamellar rather the hexagonal type that occurs in the non-super fatted system. This lamellar phase significantly increases the soluble phase volume and leads to reduction of the bar material hardness. The solid phase is also significantly different from non-super fatted solid phase. In addition to the solid phases of non-super fatted soap mixture a variety of acid soap and fatty acid phase may also potentially occur. The final solid phase is strongly dependent on the temperatures at which the shear/mixing is applied to the system during processing.

Soap In-use Properties and Recrystallization. The soap bar in-use properties such as hardness, hydration and wear rate, mush layer and lather volume, etc, are influenced strongly not only by the crystalline phase structure (including the liquid crystalline phase) but also by the shape and size of the crystalline phases. These influences are strongly dependent on the formulations, the processing methods, ie, high or low shear, and the processing temperatures.

Hydration of soap bar material occurs when the soap contacts water during washing and also after washing as water is left on the bar surface. The hydration takes place usually via two different mechanisms, ie, capillary flow and diffusive flow. In the first process water flows into the porous structure, which is created by water evaporation from the bar surface during storage period, owing to capillary forces, and the porous bar surface is rapidly rehydrated to its original water content (as processed). In the latter process the now nonporous bar hydrates further by a molecular diffusive flow which principally involves soap and water. This much slower process is responsible for the observable mush layer which develops when the bar is immersed in water for an extended period.

The phase changes during the hydration process involve the dissolution of the eta type solid-phase phases to form additional liquid crystal and solution phases. The less soluble kappa phases that contain longer chain soaps also dissolve and the long chain soaps then reprecipitate as insoluble solids. These solids along with the liquid crystalline phases are responsible for the mush layer which forms on the bar surface.

Lather volume depends upon the amount and the type of soap dissolved in the soap liquor during lathering. The mobility of the soap molecules, in addition to their surface properties, contributes to foaming. It is therefore possible that the soaps with very short chains (sodium caprylate and sodium caprate) may have an additional lather benefit. However, the proposed benefit should be restricted to low wash temperatures. The source of the short-chain soaps is the coconut or palm kernel oil component of the fat charge. The amount of soap in solution in the wash liquor increases as the level of soluble soap in the bar increases. However, because the lather depends on the very short transient hydration period, it is the amount of soap which goes into solution over this period that is important. This amount also increases as the rates of dissolution of the solid soluble phases of the bar structure increase.

The absolute amount of soluble soap in the bar depends on the blend of oils used (fat charge) and the total fatty matter of a formulation. The rates of solution of soluble soap increase as: (*1*) The physical size of the abraded soap particle decreases; (*2*) The mixing of the soluble particles becomes more intimate at the colloid level; and (*3*) The soap concentrations in the liquid crystalline and solution phases increase; the maximum soap concentrations in these liquid phases influence the rates of abrasion of soap from the bar and the rate of dissolution in the wash liquor respectively.

Small particles (a few microns) of finely mixed liquid crystalline and eta solid will dissolve with sufficient rapidity to be fully utilized during the short lathering time.

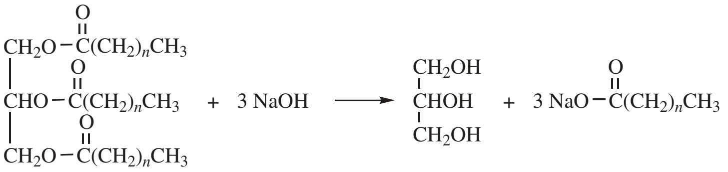
However, some of the soluble soap bound in small kappa type particles or larger soluble agglomerates is unlikely to be released in this time. The acid soap kappa phases are even more wasteful in this respect. Thus, apart from increases brought about by variations in the fat charge and total fatty matter, lather is increased by an intimate mixing of all soaps on the colloidal structural level and a separation of insoluble from soluble soaps at the molecular level. The production of an optimum bar structure has to be balanced against the deleterious effect of lowering the total fatty matter. It can only be stated that any benefit in lathering properties from such a formulation change will be most clearly seen in certain well processed super-fatted formulations.

Any increase in process temperature can have a deleterious influence on lather for any formulation if it leads to an increase in particle size. However, processing temperature is particularly important for the temperature sensitive super-fatted formulations. This sensitivity results from the additional extreme changes in structure that results from the processing temperatures.

While an increase in the electrolyte concentration in a soap liquor will always cause some reduction in lather it is believed that the gross reduction in lather often observed in high-electrolyte bars stems more from the influence of electrolyte on the types of solid soap phase content of the bar structure than from any subsequent influence which electrolyte may have on soap liquor properties.

3. Raw Materials and Their Processing

3.1. Principal Raw Materials. Carboxylate soaps are most commonly formed through either direct or indirect reaction of aqueous caustic soda, ie, NaOH, with oils and fats from natural sources, ie, triglycerides. Oils and fats are typically composed of both saturated and unsaturated fatty acid units containing between 8 and 20 carbons randomly linked through ester bonds to a glycerol [56-81-5] backbone. Overall, the reaction of caustic soda with triglyceride yields glycerol (qv) and soap in a reaction known as saponification. The reaction is shown in equation 1.



$$\begin{array}{l} \mathrm{CH_2O-\overset{O}{\overset{\|}{C}}(CH_2)_{\mathit{n}}CH_3} \\ | \\ \mathrm{CHO-\overset{O}{\overset{\|}{C}}(CH_2)_{\mathit{n}}CH_3} \\ | \\ \mathrm{CH_2O-\overset{O}{\overset{\|}{C}}(CH_2)_{\mathit{n}}CH_3} \end{array} + 3\,\mathrm{NaOH} \longrightarrow \begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array} + 3\,\mathrm{NaO-\overset{O}{\overset{\|}{C}}(CH_2)_{\mathit{n}}CH_3} \qquad (1)$$

Saponification can proceed directly as a one-step reaction as shown above, or it can be achieved indirectly by a two-step reaction where the first step generates fatty acids through simple hydrolysis of the oils and fats and the second step forms soap through the neutralization of the fatty acid with caustic soda. There are practical considerations which must be addressed when performing this reaction on a commercial scale. Compositional differences in the oils and fats give rise to their significantly different physical properties and those of the resulting fatty acids and soaps. The main compositional difference is the chain length distribution of the fatty acids associated with the oils or fats.

3.2. Fats and Oils Used in Soap Making. Oils and fats used in soap making have traditionally been classified as either lauric or nonlauric oils/fats. A typical toilet soap will contain a blend of both of these types of oils and fats. This broad classification is based on the fact that oils and fats tend to contain either extremely low levels of C_{12} alkyl chain material or high levels (typically ca 50% by weight). The lauric oils are relatively rare commercially with only two (coconut and palm kernel oil) accounting for the bulk of lauric oil use in soaps world-wide. The nonlauric oils are numerous but again there are two that account for the bulk of nonlauric use in soaps world-wide, these being tallow and palm oil. Many soaps also contain blends of nonlaurics with either tallow or palm oil being blended with harder materials such as palm stearines or softer oils such as soya bean. Examples of typical chain length distributions of a number of commonly used oils and fats for toilet soaps are given in Table 1 along with their measured iodine value (IV). The latter is a measure of the degree of unsaturation of the oils and fats. Although this is a single number it can be used to predict the effects of individual or blends of oils and fats on the hardness of a soap blend.

The lauric oils shown in Table 1 all have similar levels of C_{12} with only minor differences in other chain lengths. None contain high levels of C_{16} or C_{18} in the form of saturates or unsaturated materials. In contrast the two main nonlaurics (tallow and palm) contain only low levels of short chain lengths (ie, <=C12) and have high levels of C_{16} and/or C_{18} as both unsaturated and saturated materials. A key point to note is that an oil name defines the general chain lengths present, but there is some variability in quantities of individual chain lengths; an example of this effect is shown in Table 1 for tallows sourced from South America and the UK. Other sources of nonlauric oils are of two types; hard and soft oils. The hard oils are classed as stearines and are produced either by fractionating tallow or palm or by hardening oils or fats. The extent of this hardening is defined by their iodine value; the lower the IV, the harder the material. An additional consideration for oils and fats which have been hardened catalytically is that some trans-esterification of the double bonds often occurs. The resulting trans-isomers produce soaps with markedly different solubilities from their cis-isomers, which must be taken into consideration during blending for achieving acceptable processing and in-use properties.

Toilet soaps manufactured by extrusion require both minimum and maximum product hardness and this imposes limits on the level of soft and hard oils and fats that can be used in a blend. However blending of soft and hard oils can achieve the target hardness and it is obvious that many combinations of oils and fats could be produced to meet this requirement. In addition to the process requirement of product hardness, there are a number of product in-use properties which influence the choice of the oil and fat blend. These variables are quite numerous, but the main ones can be summarized as (*1*) lauric oil content which controls lather and (*2*) the amount of unsaturated chain lengths, which due to their high water solubility can improve speed of lather generation but can also negatively affect bar economy if they are present at too high levels. Conversely, high levels of stearines that are relatively insoluble in water can improve bar economy, but can reduce lather if present at too high a level. The main factor limiting soft oil use is the chemical instability of the unsaturated chain lengths, particularly for di-, tri- and polyunsaturated materials. The blending of oils and fats to achieve the target hardness for processing and acceptable in use properties is, thus, a complex balancing operation. One widely employed approach is to use the blend iodine value, in combination with a constant level of lauric oil to identify blend options that will have similar process and in-use behavior. A final consideration is the chemical state of the oils and fats. The effects of storage conditions, impurities and processing can lead to significant differences between nominally identical oils or fats and this is usually reflected in an industry-standardized specification known as a grading value being associated with an individual oil or fat. This in turn influences the oil price with higher grade oils and fats being more expensive, but having less undesirable effects on product properties such as color and odor. This overall approach allows manufacturers to select blends of oils and fats to minimize raw material costs while maintaining processing and product user properties.

In the last ten years the increased use of chemical splitting of oils and fats has widened the range of feedstocks for soap making to include “non-natural” chain length blends. This provides soap makers with additional opportunities to cost optimize their blends. A further consequence of this is that soaps made from distilled fatty acids tend to contain lower levels of impurities which in natural oils and fats can have deleterious affects on color and odor. This offers the potential for further cost savings by reduction in levels of minor ingredients such as whiteners and antioxidants.

Other Sources. The most commonly used oils and fats in soap making around the world are tallow, palm oil, and their stearines and the two lauric oils, coconut and palm kernel oil. However over the years local shortages in these oils and fats have led to a plethora of alternative oils/fats being used as nonlauric and lauric oil substitutes. For instance until the 1990s, India relied on blends of local oils such as linseed, rice bran, and castor which with appropriate hardening, dehydroxylation, etc could produce a nonlauric blend that mimicked the process and in use behavior of palm oil. Similarly in South America partially hardened soya bean oil has been used as a partial replacement for tallow. Other oils/fats occasionally used as nonlauric replacements include lard (pig fat) and a number of soft oils such as sunflower and groundnut oil. Alternatives to the common lauric oils are extremely limited but include rosin and a range of synthetic surfactants (18).

3.3. Raw Material Pretreatment. The quality, ie, level of impurities, of the crude oils and fats used in the manufacture of soap is important in the production of commercial products. Oils and fats are isolated from various vegetable and animal sources and contain different intrinsic impurities although both will contain free fatty acids and mono and diglycerides. These crude oils and fats typically contain a range of nonsaponifiable contaminants some of which affect color and odor of the oil or fat and also that of the finished soap product. For animal fats these will include blood, mucilage, and other proteinaceous material, phosphatides, and bone. For plant-derived oils, typical contaminants include sterols, carotenoids, phosphatides, tocopherols, etc. In addition both will contain physical dirt, water, rust, and other material picked up during their extraction and storage.

For commercial soaps, it is desirable to keep these impurities at the absolute minimum for both storage stability and finished product quality considerations.

There are a number of processing steps that can be used to improve the quality and stability of the oils and fats raw materials. These include water washing, alkali refining, physical (steam) refining, deodorization, bleaching, and hydrogenation. Water washing, also called degumming when dealing with vegetable oils, is an effective means of improving the color of oils and fats through the elimination of proteinaceous solids, phosphatides, and other water-soluble impurities. Hot water, possibly containing some phosphoric acid or sodium phosphate, is mixed with the oils or fats. The water layer is allowed to separate either statically or by using centrifugal force. Many of the solids and other impurities become either solubilized or suspended in the water and removed. Alkali and physical (steam) refining can be utilized to decrease the amount of free fatty acid and other color bodies present in oils and fats. Alkali refining washes the oils and fats with alkaline water and converts fatty acids into soap. The resulting soap is removed with the alkaline aqueous phase through settling or centrifugation. In physical refining, volatile impurities including low boiling fatty acids are vaporized and removed from the oils and fats by steam-heating the material. Deodorization, also called steam stripping, is another steam distillation process. For deodorization, however, the distillation is performed under vacuum that allows for more efficient removal of the less volatile odour bodies. Bleaching is most commonly done using a physical adsorption process in which activated clay, eg, fullers earth, is slurried with the dry oil under vacuum at temperatures around 90°C. The color bodies adsorb onto the clay, which is subsequently removed through a filtration process at a lower temperature to minimize oxidative damage. Hydrogenation is also frequently utilized in the processing of oils and fats to improve their storage stability through reduction in the amount of polyunsaturates and unsaturates present. This is achieved by contacting the oils and fats in a reactor containing a catalyst, eg, Ni or Pt, and hydrogen gas under pressure so that hydrogen adds across the double bonds.

Industry uses a number of analytical methods to characterize oils and fats, in terms of a number of parameters which include moisture, titre (solidification point), free fatty acid, unsaponifiable material, iodine value, peroxide value, and color. Moisture content of the oils and fats is an important measure for storage stability at elevated temperature because it facilitates hydrolysis which in turn impacts odour and color quality. Titre is a measure of the temperature at which the material begins to solidify, signifying the minimum temperature at which the material can be stored or pumped as a fluid. Free fatty acid is a measure of the level of hydrolysis the oils and fats have undergone. Increased fatty acid content usually negatively impacts product color stability because fatty acids are more susceptible to oxidation. Unsaponifiable material is a measure of the nontriglyceride fatty material present, which affects the soap yield of the material. The iodine value is a measure of the amount of unsaturation present in the oils and fats. Peroxide value is a measure of the amount of oxidation the oils and fats have undergone and indicates the potential for further degradation.

4. Base Soap Manufacture

4.1. Direct Saponification of Oils and Fats. Direct saponification of oils and fats is the traditional process utilized for the manufacturing of base soap. Commercially this is done through either a kettle (pan) boiling batch process or a continuous process. In both cases there are three key stages required to produce a neat soap, (lamellar liquid crystal containing ca 70% soap) suitable for further processing into bar products. These stages are saponification, washing and fitting.

Kettle Boiled (Pan) Process. This process produces soap in large, open steel tanks known as kettles or pans, which can hold up to 130,000 kg of material. Kettles are cylindrical tanks with conical bottoms, which contain open steam coils for heating and agitation. The traditional batch making process carries out the three essential stages, known as saponification, washing, and fitting in the same vessel. To initiate the saponification, oils and fats, caustic soda, salt and water are simultaneously added to the kettle. Effective mixing is important in this process because of the low miscibilities of the oils and fats and caustic lye. The addition of steam to the system facilitates mixing and the saponification reaction. In some systems, the reaction is enhanced through the use of specially designed saponification jets, which allow for intimate mixing of the two components during the charging of the kettle. Care must be taken when blending the oils and fats with caustic soda, salt, and water to ensure a consistent reaction rate for forming the desired neat soap. It is common practice to leave some previously formed soap in the kettle before charging the kettle with the new batch of saponification. This soap, through its surfactant properties, helps disperse the fats and oils and water phases through better emulsification, thus, increasing the reaction rate. To complete the saponification process, the soap batch is boiled for a period of time using steam sparging (via open steam coils).

Upon completion of the saponification reaction, additional salt is added to the kettle while boiling with steam to initiate the washing stage by converting the single phase neat-soap (lamellar liquid crystal) into a two-phase lamellar liquid crystal-aqueous lye composition. This process is also called opening the grain of the soap. The lye layer (located at the bottom of the kettle) is an aqueous phase containing a high level of salt, glycerol, and only small amounts of soap due to its low solubility in saturated salt solution. This two-phase mixture is allowed to separate for several hours, after which the aqueous solution (lye) is removed from the bottom of the kettle. This lye contains most of the glycerol produced during the saponification process and can be transferred to a glycerol recovery system, where the glycerol is recovered, purified, and used for other purposes. It is common to use several washing stages to optimize glycerol removal. The soap remaining in the kettle now contains a high level of salt and so a fitting stage is initiated. This stage involves the addition of dilute caustic soda solution to the soap. This mixture is then given time to separate into two layers, with a pure neat soap at ca 70% concentration in the upper layer containing only low levels of salt and glycerol and other impurities. The lower layer (nigre), will contain most of the salt and any water-soluble colored impurities. After separation of the nigre layer, the upper neat soap is ready for further processing via drying and finishing. This overall three-stage kettle process requires considerable practical expertise, is time-consuming and requires several days to complete.

4.2. Continuous Saponification Process.

There are a wide variety of commercial systems for continuous soap-making; details of a number of these and their operation are given in the references (3). However all rely on high speed saponification using intense mixing followed by separate units to continually wash and fit the soap to produce the desired neat soap required for further drying/ finishing. All of these routes are less labor intensive and faster than the previous batch process and hence provide improved manufacturing efficiency. An example of a typical continuous saponification process is given in Figure 3. Although commercial systems may differ in design aspects or specific operations, they all saponify fats and oils to finished soap using the same general process (Fig. 3).

In the system shown in Figure 3, blended oils and fats feedstocks are continuously and accurately metered into a pressurized, heated vessel, commonly referred to as an autoclave, along with the appropriate amount of caustic, water, and salt. The concentrations of these ingredients are adjusted to yield a mixture of neat soap and a lye phase. At the temperatures (~120°C) and pressures (~200 kPa), the saponification reaction proceeds quickly (<30 min). A recirculation system ensures a residual level of soap in the autoclave to improve contact between the oil and water phases and provides additional mixing. After a relatively short resident time in the autoclave, the neat soap and lye phase reaction blend is pumped into a cooling mixer where the saponification reaction is completed and the reaction product is cooled to below 100°C. The reaction product is pumped next into a static separator, where the lye phase containing a high level of glycerol (25–30%) is separated from the neat soap through gravitational force or settling. The neat soap is then washed with a lye and salt solution using a counter-current flow process. This process is often done in a vertical column, which might be an open tube or contain mixing or separation stages. The neat soap is introduced into the bottom of the column and the lye/salt (washing) solution is pumped into the top. The less dense neat soap rises up in the column while the lye/salt solution falls to the bottom. The washing solution removes impurities and allows for further collection of the glycerol. As with the kettle process, it is important to have a proper level of electrolyte (salt and lye) for effective removal of the glycerol. Final separation of the lye layer from the neat soap is commonly achieved using centrifugation. After centrifugation, the remaining caustic or residual alkalinity in the separated neat soap is neutralized through the accurate addition of fatty acid in a steam-jacketed mixing vessel (crutcher). The soap is now ready for use in the manufacturing of soap bars.

4.3. Fatty Acid Neutralization Process. This route produces soap via a two stage process. In the first stage (hydrolysis) the oils and fats are split into fatty acids using steam/water and separated from the glycerol and other impurities. These fatty acids can then be blended if necessary to the target soap charge required and then neutralized in the second stage with alkali. This process normally produces a neat soap, which is then dried and finished using identical processing to the conventional direct soap-making route previously described. Typical operating details of these two process stages are as follows:

Hydrolysis Step. The hydrolysis of oils and fats by water requires intimate mixing of these two normally immiscible phases. The reaction is carried out under conditions where water possesses appreciable solubility (10–25%) in oils and fats. In practice, this is achieved under high pressure 4–5.5 MPa (580–800 psi) and at high temperatures (~240–270°C) in stainless steel columns of around 24–31 m in height and 50–130 cm in diameter (Fig. 4). ZnO is sometimes added as a catalyst to the feedstock oils and fats to facilitate the reaction. The oil and fat feedstock is injected at the bottom and water is injected at the top of the column. The columns may be either open in design, or contain baffles to ensure better mixing through turbulent flow. High pressure steam inlets are placed at three or four different heights in the column for heating. This design establishes a countercurrent flow pattern with the water moving through the column from top to bottom and the oils and fats in the opposite direction. As these materials intermix at the high temperatures and pressures employed, the ester linkages in the oils and fats hydrolyze to liberate fatty acids and glycerol. The newly formed fatty acids continue to rise up the column, while the resulting glycerol is carried (washed out) downward with the water phase. Because this is a reversible reaction, it is important to remove the glycerol from the mixture through the countercurrent washing process. The concentrations of glycerol and glycerides (mono, di, and tri) are lowest and the concentration of fatty acid is highest toward the top of the column.

The rate-limiting step in the process is the removal of glycerol from the fatty acids. This removal relies on interaction with the wash-water falling through the column. The Zn-soap formed by the reaction of ZnO and fatty acid acts as a phase-transfer catalyst, improving the transfer of glycerol from the oil to the water phase. The separation of the glycerol and fatty acid in the column prevents the reverse reaction from occurring. The hydrolyzer process provides around 99% efficiency for the conversion of the oils and fats to fatty acids and glycerol, and requires around 90-min residence time.

The fatty acids that emerge from the top of the column contain entrained water, partially hydrolyzed fat, and the Zn-soap catalyst. This product stream is passed into a vacuum dryer stage where the water is removed through vaporization and the fatty acid cooled as a result of this vaporization process. The dried product stream is then passed to a distillation system.

The distillation system allows for improved fatty acid quality, ie, odor and color, through the separation of the fatty acid from partially saponified fats and oils, the Zn catalyst, and color and odor bodies. This is achieved by heating the product stream in a heat exchanger to around 205–232°C and introducing it into a vacuum chamber (flash still) at 0.13–0.8 kPa (1–6 mm Hg) absolute pressure. The fatty acids are vaporized under these conditions and removed from the undesired materials such as the partially hydrolyzed triglyceride. The vaporized fatty acids are then passed through a series of cold water condensers for fractionation and collection. Systems vary in the number of condensers but a three-condenser system is common. The fatty acids are typically separated into a heavy cut, a mid-cut, and a very light cut. Depending on the end uses for the fatty acid, these fractions may be used as separated for speciality fats such as stearic acid or reblended for desired fat ratios such as 80:20% tallow : coconut soap. The light cut is often removed from the other condensates because it contains many of the odor bodies present in the fatty acid.

The fatty acids obtained from the process can be used directly or further manipulated for improved or modified performance and stability.

Neutralization Step. The formation of soap from fatty acids is achieved through the reaction of the fatty acid with the appropriate caustic. This reaction is extremely rapid for most common caustics, eg, NaOH or KOH, and requires proper stoichiometry and rigorous mixing to ensure processing effectiveness. Although this appears relatively straightforward, in practice, there are a number of processing considerations which must be addressed. First, an exact ratio of fatty acids, caustic, water, and salt must be maintained to ensure formation of the desired neat soap phase. The process is controlled to avoid the formation of middle soap, which has a high viscosity and does not disperse rapidly, or the formation of a neat soap-nigre biphasic mixture, which may separate upon storage. Second, intimate mixing of the oil and aqueous reactants is necessary to ensure uniform neat soap phase composition. Third, because of the heat liberated by the reaction, temperature control must be maintained within certain limits to prevent overheating and boiling/foaming.

There are a variety of commercial systems for achieving neutralization. Generally, a heated fatty acid blend (~50–70°C) and caustic-salt-water (~25–30°C) streams are metered into some form of a high shear mixing system, commonly referred to as a neutralizer. The mixed stream heats to between 85 and 95°C on account of the latent heat of reaction and is pumped into a receiver tank which effectively mixes the soap through both a recirculation system and agitation. After a short residence time in the receiver tank to ensure a uniform composition, the resulting neat soap is pumped into storage tanks or to the finishing operations.

Comparison of Base Soap Manufacturing Routes. Direct saponification of oils and fats is well known, characterized, and straightforward; requires conventional equipment; and is relatively energy-efficient. However, it imposes practical limitations with regard to changes in the oils and fats ratio desired for finished soap bar formulations. Furthermore, direct saponification has the drawbacks of lower glycerol yields, limited flexibility toward formation of mixed counterion soaps, and requires higher quality feedstock for good quality soaps. In contrast, the hydrolyzer/neutralizer system is more flexible with regard to formation of mixed counterions and formula changes and provides better glycerol recovery. In addition, the ability for both distillation and post-hardening provides greater flexibility in oils and fats feedstock selection; lesser grades can be utilized to yield comparable quality base soap. However, this process is extremely energy-intensive and requires more specialized process equipment, eg, hydrolyzer columns, stills, a hydrogenation system, and neutralizer, and necessitates the use of stainless steel on account of the corrosive nature of fatty acid.

5. Formulation

The formulation of bar soaps has become increasingly complex with changing consumer bathing habits and expectations. In the past, consumers' bathing habits were such (eg, once-a-week baths) that simple lye soaps were acceptable. However, it is not uncommon nowadays to shower everyday, which puts greater demands on the performance properties of a soap bar, for example, mildness to skin and prevention of bathtub ring (19). Manufacturers of bar soaps have developed a variety of formulation approaches to deliver products that better meet current consumer needs. This is achieved through the proper balancing of soap components, inclusion of various additives, or the blending of synthetic surfactants into the formula. In addition, new forms of cleansing products have been introduced to address these changing habits and consumer needs, eg, liquid handsoaps and shower gels or body washes. For personal cleansing products, including bar soaps, performance is measured by such tests as amount and creaminess of lather, wet cracking, economy, water uptake (mush), rinsability (the amount of residue left on surfaces after rinsing with hard water), and mildness to skin (20,21). It is through use of these measures and exhaustive consumer research that modern soap-makers develop better products for consumer needs.

5.1. Soap Bars.

In soap bars, the primary surfactant is predominantly sodium salts of fatty acids. These products typically contain between 70 and 85% soap. Occasionally, potassium soap (~5–30%) is included in the formulation to increase the solubility of the soap and, hence, the bar's lathering properties. The low Krafft temperatures for potassium soap are the basis for the lather enhancement, but also limits their content in bars, making them softer and poor in economy.

Soap performance can be controlled through the proper blending of oils and fats to specific ratios, and the formation of the proper phase and colloidal structure. It is common to produce soap using a blend of tallow or palm and coconut or palm kernel oils, generally in a ratio of between 85:15 and 50:50. As the amount of coconut oil is increased in the bar, the lathering profile of the product typically increases as a result of the inherent higher solubility of the soaps formed from coconut (shorter chain length soaps). However, this higher lather comes at the expense of poor economy and increasing water uptake which results in the formation of an expanding outer soft layer known as mush, which increases for the same solubility reasons. Furthermore, the higher content of sodium laurate in these high coconut soaps can negatively impact the mildness of the product, because laurate soaps are intrinsically more irritating to skin than other chain lengths (22).

Additionally, soap bars typically contain between 8 and 20% water, 0.5 to 1% NaCl, and low levels of glycerol. Both salt and glycerol modify the processability of soap during milling and plodding, as well as being carryover ingredients from the manufacture of the base soap. Similarly the water content is critical in controlling bar hardness and hence processability.

5.2. Bar Soap Additives.

There are a variety of additives that may be formulated into soap bars to provide additional consumer benefits or modify the performance of the products. In all cases a key consideration must be the mode of addition of the additive. If additives are mixed using low shear then it is likely that they will exist within the product as macroscopic domains and as such will not impact the overall bar soap phase chemistry. However the presence of such large defects is liable to disturb bar macrostructure and produce effects ranging from bar cracking, insoluble lumps, uneven bar wear and poor economy. The actual behavior will depend both on the physical nature and chemistry of the additive and its domain size in the bar. Conversely if the additive is mixed using high shear then it has the potential to disturb the soap phase chemistry which is liable to impact all of the aforementioned bar properties, but the magnitude and type of effect will be different for any particular additive.

Free Fatty Acid. Soap bars are intrinsically alkaline in nature on account of the physical properties of soap in water and the process utilized in its manufacture, which yields base soap having a very slight excess of free caustic. Low levels of free fatty acid are often added to the neat soap prior to drying to neutralize this slight excess of caustic. These low levels have no effect on processability or in-use properties. However, addition of higher levels of free fatty acid provided they are molecularly mixed into the soap, typically in the range 2–10% can significantly affect processability and in-use properties. This approach is known as super-fatting and this term was even used in advertising for Lux soap in the 1950s with the slogan “Super-fatted Luxury”. The basis for this claim is that the addition of fatty acids (usually as coconut or palm kernel fatty acids) leads to an increase in both the amount of lather and its creaminess. However a downside of this is that if processing temperature is not carefully controlled, both bar economy and water uptake (mush) can increase, the latter leading to extremely soft bars. These changes in behavior are due to a number of changes in soap phase chemistry including increased liquid-phase content and changes in the soap chain-length distribution of the crystalline solids present. To achieve optimum in-use properties the soap/fatty acid blend must be sheared during processing under controlled temperature. This is a major problem for conventional soap finishing lines where high shear usually leads to a significant temperature increase if throughput is not reduced. One novel solution to this problem pioneered by Unilever is to utilize cavity transfer mixers in the finishing line which not only deliver high shear but also have excellent heat transfer characteristics, hence accessing the desired soap microstructure while maintaining throughput (23).

If free fatty acids are added to soap without being molecularly mixed, the resulting soap bars will have a gritty feel and will wear unevenly, and will not exhibit any improvements in lather. However, irrespective of the degree of mixing, the presence of high levels of free fatty acids can also decrease the odor and color stability of the final product because oxidative degradation of fatty acids is faster than for the analogous soaps.

Glycerol. Although glycerol is normally present at low levels in soap due to incomplete removal during the soap-making process, it is often added to soaps at higher levels either to support skin-mildness claims based on its known humectancy or to promote bar translucency. For example glycerol, at levels of 10%, has been shown to change significantly the consumer skin softness and smoothness perception (24). Similarly levels in the range 5–10% are often used in milled translucent soaps. However, care must be taken when adding glycerol at such levels because it can severely affect both bar processability, bar appearance and in-use properties. For example if the glycerol is not molecularly mixed with the soap (low shear mixing process) the soap mass will be soft and sticky, producing problems during extrusion and stamping operations. The resulting bars will also have a tendency to crack and exhibit uneven wear during use. In contrast if the glycerol is molecularly mixed with the soap, the mass will be hard and slightly translucent. In this case if translucency is not required, higher levels of opacifier may be needed. The bar in-use properties will now exhibit increased water uptake (mush), due to the lower water activity which at high humidities can cause unsightly bar swelling. These effects also occur when other polyols are included such as sorbitol and sugars.

Perfume. A key aesthetic for consumer acceptance of personal cleansing products is how the product smells. Perfume is utilized by manufacturers of soaps as one of the primary means of targeting products for specific user groups and connoting different product marketing positions. A secondary purpose of perfume is to mask the fatty base odor of the soap. Product odor instability results from both the loss of perfume during storage and the propensity for oxidation of perfume and soap components. Hence, a product may change from an acceptable to an unacceptable odor profile during its lifetime if not properly formulated.

Commonly, perfume development is performed by perfume houses who focus their development on product appeal needs. For example, perfumes used for deodorant products tend to be impactful and residual to skin to provide long-lived perfume on skin. A number of products are appearing on the market that are designed for individuals with sensitive skin. The perfume levels used in these sensitive-skin products are usually lower than for other soaps and are selected to mask the base odor of the soap while providing some soft perfume notes during use, reinforcing their mildness to or compatibility with skin. Irrespective of market position, perfume levels in soaps are typically in the range of 0.2 to 1.5%.

The perfume is usually added during the finishing operation using a low shear device although in some products, a high shear stage may occur later in the finishing operation. However the effect of perfume on processing is always to make the soap mass slightly softer. The effect of perfume on in-use properties is also negligible.

Minor Ingredients. It is quite common to modify the appearance or aesthetic properties of bar soaps through the incorporation of various opacifiers, fluorescers and dyes. The most commonly used material is titanium dioxide, which at low levels (<0.8%) is an effective whitener and opacifier. Most marketed bar soaps contain some level of TiO_2 as either an opacifier in conjunction with other colorants or fluorescer as a whiteness booster. A variety of dyes are also utilized in addition to TiO_2 to generate desired product colors. The dyes used are almost exclusively dyestuffs of Drug and Cosmetic or Food, Drug, and Cosmetic grades. Some producers also utilize inert, inorganic pigments for product coloration. Pigments have an advantage over dyes; they are inherently more color-stable and not water-soluble. The latter attribute is important for striped or two-toned products, because water-soluble dyes can migrate in the product and eventually lessen the contrast between the two tones present. All of these materials are commonly added into the soap during the finishing operation.

Soaps, fatty acids, and perfumes are susceptible to oxidation during ageing (25). The oxidation process is quite complex but typically results from the reaction of the unsaturated bonds in these components with oxygen in the air, resulting in the formation of shorter chain length acids, aldehydes, and ketones which are extremely odoriferous. In the case of perfume components, oxidation can produce a change in product odor character and cause discoloration of the bar. To minimize the oxidation of the base soap and other minor ingredients in soap bars, both chelants and antioxidants are commonly used.

Chelants at concentrations of 0.1 to 0.2% improve the oxidative stability through the complexation of the trace metal ions, eg, iron, which catalyze the oxidative processes. Examples of the chelants commonly used are pentasodium diethylenetriaminepentaacetic acid (DTPA), tetrasodium ethylenediaminetetraacetic acid (EDTA), sodium etidronate (EHDP), and citric acid. Magnesium silicate, formed in wet soap through the reaction of magnesium and silicate ions, is another chelant commonly used in simple soap bars. All of these chelants are usually added into the neat soap prior to the drying operation.

Antioxidants are also used in conjunction with chelants to further improve product odor and color stability. Antioxidants work by chemically trapping the free radicals formed during the oxidation process, significantly decreasing the rate of the degradation reaction. This is particularly important for perfume components. Butylated hydroxytoluene (BHT), one of the most commonly utilized antioxidants, is usually incorporated at levels of 100–200 ppm in the formulation. BHT is frequently added directly to the perfume to improve the storage stability of the neat material. The levels of all of these materials are so low that they have negligible effect on processability and bar in-use properties.

Mildness and Skin Additives. The increased frequency of bathing and the changing consumer need has necessitated the development of products having skin care benefits. In addition to the two most common additives, fatty acid and glycerol, there is a wealth of other additives which are frequently used. Examples include lanolin, vitamin E, aloe vera gel, mineral oil, and baking soda.

Inert materials are sometimes used in soap bars as a means of improving the skin mildness of the product by decreasing the level of soap and surfactant in the bar. The cleansing agents at high concentrations can sometime dry and irritate skin. A variety of inert materials, both inorganic and organic, has been reported in the literature, including oatmeal, dextrin, starch, wax, and talc (26). These materials may also deposit on the skin during washing, further modifying the rinsing properties of the soap bar and impacting the consumer perception of the product and its aesthetic properties.

Newer technologies have been used in the manufacture of bar soaps, which truly improve the clinical mildness-to-skin of these products. One approach relies on minimising the overall levels of the more irritating soap species such as the laurates and unsaturated species through appropriate balancing of feedstocks (27,28). Another approach is the incorporation of quaternary amine compounds into the formula, which effectively complexes the soap during the wash-rinse process, reducing its potential to remove oils from or interact with the skin. The amines commonly take the form of cationic polymers based on natural materials such as cellulose, guar gums, and proteins (29).

Much of the development of new soap bar technologies has been focused on products containing some level of synthetic surfactants. The primary benefits of synthetic surfactants over soaps are their intrinsic lower sensitivity to water hardness, which improves their rinsing profiles, their lathering ability, and their effects on skin feel and mildness. Anionic, nonionic, and zwitterionic surfactants have all been formulated into bar soaps. In most bar soaps, the synthetic surfactant serves the purpose of a secondary surfactant modifying the lathering, rinsing, or skin effects profile. A major challenge has been how to incorporate relatively high levels (ie, $>10\%$) of these highly soluble synthetic surfactants into soap bars without significantly affecting both processability and in-use properties and this need has produced numerous patent filings covering specific approaches (30).

Anionic surfactants are the most commonly used class of surfactant. Anionic surfactants include sulfates such as sodium alkylsulfate and the homologous ethoxylated versions, sodium monoglycerol sulfate and also the sulfonates, eg, sodium alkylglycerol ether sulfonate and sodium cocoyl isethionate.

Nonionic surfactants include the alcohol ethoxylates, ie, $HOCH_2CH_2O(CH_2CH_2O)_nR$ and also the sugar-based surfactants such as alkyl polyglycosides. Zwitterionic surfactants, such as cocoamidopropyl betaine and cocoamphoacetate, are more recent surfactants in the bar soap area and are typically used at low levels ($<2\%$) as secondary surfactants. These materials can have a dramatic impact on both the lathering and mildness of products (31).

These surfactants, in conjunction with soap, produce bars that may possess superior lathering and rinsing in hard water, greater lather stability, and improved skin effects. Beauty and skin care bars are becoming very complex formulations. A review of the literature clearly demonstrates the complexity of these very mild formulations, where it is not uncommon to find a mixture of synthetic surfactants, each of which is specifically added to modify various properties of the product.

An extension of the soap-coactive approach has been the production of ultra-mild bars which contain only low levels of soap, with the primary surfactant being a synthetic anionic. The first product of this type was Dove, which contained sodium cocoyl isethionate as the primary surfactant. More recently modified versions of this formulation have appeared containing milder coactives (eg, cocoamidopropyl betaine) and an emollient such as stearic acid (32). Such benefits come at a cost to the consumer because these materials are considerably more expensive than simple soaps. Attempts to extend this approach using alternative synthetic anionic surfactants have been less successful. This is mainly due to the poor crystallinity of many synthetic anionic surfactants which even in their anhydrous state are soft pastes as opposed to crystalline solids, making them unsuitable for use at high levels in bar products.

One common theme throughout all of these products and patent filings is that the synthetic surfactant(s) are always molecularly mixed with the other product components. Failure to ensure the formation of a homogeneous product results in major processing problems and poor product in-use appearance and behavior.

Antimicrobial Agents. Antimicrobial agents have been used for a number of years in soap bars as a means of providing additional deodorant protection through their residual effectiveness on suppressing the growth of odor-causing bacteria. These materials may deposit on skin during the washing process and provide a reservoir of active ingredient that is effective at suppressing bacterial growth between washings. It is widely believed that these soaps may provide additional benefits on account of their ability to control the microflora on the skin surface. One such benefit may be the reduction in the level or frequency of minor skin infections by controlling the *Staphlyococcus aureus* level on the skin surface (33). Only two active ingredients are commonly used in bar soaps: trichlorocarbanalide or TCC (Triclocarban) and trichlorohydroxydiphenyl ether or TCS (Triclosan). These compounds are typically used at concentrations of 0.25 to 1.5% in the final product and have activity against a wide range of micro-organisms. They are usually added using low shear and have no effect on either processability or product in-use properties.

5.3. Speciality Soaps. There are a variety of speciality soaps that require certain additives to deliver the special consumer needs for which they were developed. Examples include scouring soaps that contain an abrasive agent homogeneously distributed throughout the soap to aid in the cleaning properties of the product. The abrasives are extremely small particles of insoluble material such as pumice. Similarly encapsulated oils or perfumes can also be incorporated into conventional milled soap bars. Bars with visual effects include striated soap bars, which can be produced using two soap streams with different colorant systems that are intentionally poorly mixed during extrusion through the plodder. Alternatively a single soap stream can be used and a dye injected during extrusion. If a true striped bar is required, this can be manufactured using separately colored soap streams and a specialized extruder. The other common visual effects are translucency and transparency. Each of these has its own specific formulation space and process requirements, with the former being accessed either via a milled-process route or a cast process and the latter being accessed solely by a casting process.

Milled Translucent Soaps. A semiconventional finishing line can be used to make translucent toilet soap. The formulation and processing of these soaps differs from conventional opaque soaps in that the water content must be high (typically 14–20%) and either glycerol and/or a polyol (eg, sorbitol, sucrose) must be present at level of 4–10%. This type of formulation can also include other additives such as potassium soap. Irrespective of the exact formulation, the one additional requirement for achieving translucency is high shear. This can be achieved either by pre-blending all materials prior to drying or by utilizing a high shear device (eg, batch Z-blade mixer) during the finishing operation. If throughput is an issue, a continuous high shear mixer such as a CTM should be used (34). If a low shear finishing line is used the resulting poorly mixed mass will be soft and difficult to process into bars, and the in-use properties will be poor. In contrast, high shear processing will yield bars with good translucency, which will improve further during storage (due to moisture loss). These bars will also have acceptable in use properties although with a tendency to form thick mush layers if exposed to humid conditions.

Transparent Soaps. The early commercial transparent soap bars were based on conventional fat charges of tallow and coconut and also contained solubility enhancers such as potassium soap and rosin, in addition to glycerol and ethanol. These products were cast into molds and allowed to set and then stored for an extended period of time to allow the ethanol to evaporate. It is only after evaporation of the ethanol that transparency is achieved. This overall process can take several weeks and coupled with the alcohol evaporation is a slow and costly process. The best known product of this type still exists today and is sold by Unilever under the name “Pears soap”.

In recent times there has been much interest in this product form due to the high consumer appeal of glass-clear bars. Much work has been carried out to eliminate the alcohol evaporation stage of the process to produce a high quality bar at high throughput. This goal has been achieved by several manufacturers, using a range of formulations but in essence a single approach which is to reduce the soap content and replace this with high levels of polyols and other solvents (35). Common solvents include ethanol, propylene glycol, dipropylene glycol and triethanolamine. These are combined with blends of polyols such as glycerol, sorbitol, and sucrose. These components along with water often make up at least 50% of the product. The process involves pre-blending all ingredients at elevated temperature and pouring into molds where the product is allowed to set. The bars can then be either extracted from the mold and packaged or sold in-the-mold (36). A successful formulation is one that forms an isotropic solution at elevated temperature and does not form any liquid crystalline phases during the cooling phase. This minimizes formation of large solid crystals, which would reduce the transparency of the final product. The solvents and polyols also aid the formation of a clear product by retardation of crystal growth.

There are many examples of these types of product on the market especially in Japan where mild products based on synthetic surfactants have also been developed using the same principles outlined here. One of the best known European products is Neutragena which is based on a triethanolamine soap.

5.4. Liquid Soaps and Body Washes. In the late 1970s and early 1980s a new form of soap product emerged, commonly referred to as liquid handsoaps. These liquid soaps were offered as a practical replacement of soap bars for use at sinks in the bathroom and kitchen. Manufacturers have taken two basic approaches to the formulation of these products: soap-based and synthetic-based formulations. Soap-based formulations typically use potassium soaps which because of their high solubility are unlikely to precipitate out at low ambient temperatures. These soaps have typically been of either short-chain lengths, such as coconut soap, or a blend of short-chain lengths and unsaturated soaps such as oleic. More recently, these soap-based formulations have been replaced by synthetic surfactant-based formulations. Synthetic surfactant formulations have the advantages of being milder-to-skin, cleaner rinsing, higher lathering, and less sensitive to water hardness. A typical synthetic surfactant formulation is around 80% water and contains sodium alkylethoxy sulphate as the primary surfactant, a nonionic surfactant such as lauramide DEA, and potentially a lather-building amphoteric surfactant such as cocoamidopropylbetaine [61789-40-0] (37). The global market has evolved significantly since the initial introduction of liquid handsoaps, and most products now often contain some form of benefit agent such as an antibacterial agent (usually TCS) and/or a moisturiser (typically glycerol or a polyol).

Body washes are another more recent introduction into the marketplace. These products have become a mainstay in the global market. Body washes can be simple formulas similar to those used for liquid handsoaps or complex 2-in-1 oil-in-water emulsion, moisturising formulations. These products contain a wide range of synthetic surfactants not typically found in bar soaps or liquid handsoaps, such as sodium monoalkyl phosphate and alkyl aminocarboxylates. It is not uncommon to find over 20 different components in these formulations, with no less than six or seven different surfactants. These products can also contain skin benefit agents, such as cholesterol, fatty alcohols, fatty acids, cationic polymers, and emollient oils to provide even milder-to-skin cleansing and in-use moisturization.

6. Bar Soap Manufacture

The conversion of wet base soap into consumer-acceptable soap bars can be achieved using one of two commonly utilized manufacturing routes: castingmolding and milling-extrusion forming, both of which use a variety of processing unit operations or finishing steps. These steps include wet mixing or crutching, drying, dry mixing or compounding, and bar forming also known as finishing. A number of recent innovations in the two basic routes have been reported eg, the hot-extrusion process and the continuous casting processes, the latter of which has largely replaced the older cast-mature process.

6.1. Casting in Frame.

The most commonly used casting process is the so-called 'framed bar process'. This is by far the oldest and the most straightforward process utilized in the production of bar soaps. The wet soap base is pumped into a heated, agitated vessel commonly referred to as a crutcher. The minor ingredients used in soap bars such as fragrance or preservative are added to the wet soap in the crutcher or injected in-line after reduction of product stream temperature. The hot mixture is then pumped into moulds and allowed to cool.

These molds can be either finished bar-shape molds or large blocks. Finished bar-shape molds can be either a mated two-piece design or a five-sided, open-top design. Upon cooling the solid bar is removed from the mould and packaged as desired. For the large blocks, the mold is pulled apart and the block of solid soap is removed. Wire cutters are employed to cut the blocks first into slabs, then into stripes, and finally into rectangular bricks representing the finished size of the bar. The rectangular brick is finished by a final stamping step which typically embosses the logo and any minor shape modifications into the brick. This large-block approach is only suitable for brick-like shapes, whereas the finished bar-shape molds allow for the production of much more complex shapes.

Traditionally, this process has been utilized primarily for low cost soap bars because it produces bars with limited shape options. A derivative of this approach has been utilized for many years to make transparent bars by the so-called cast-mature process.

6.2. Cast-Mature.

The cast-mature process was an early attempt to make high quality transparent soap, with the best known product, "Pears soap". The process is similar to the framing process except for the inclusion of high levels of alcohol and the need for extending ageing times. The initial melt which is based on a semiconventional tallow : CNO blend with added solubilizers is poured into longitudinally bar-shaped molds and allowed to cool. After cooling, the opaque product is cut into individual bars and each is embossed with the logo and placed in ovens to evaporate off the alcohol. After a number of weeks the bars are removed from the oven at which stage they are transparent. The bars can then be surface-cleaned to optimize transparent appearance and packaged as for normal soap bars.

6.3. Continuous Casting.

Improvements to the basic cast-mature process appeared initially in Europe and Japan where premium quality high transparency bars were able to demand a considerable premium over conventional toilet soaps. Two major advances were made the first being the identification of new formulation spaces (35) which no longer required maturation times and the second being the automation of the process (36,38). Using these combined advances, throughputs approaching conventional milled soaps can now be achieved. A number of different machine designs exist but in all cases the same basic process is used: the hot melt is injected into individual molds, and these are then either passed through a cooling tunnel after which the bars are removed from the molds and packed or the molds act as primary packs in which case these are simply sealed and allowed to cool/set post-processing. In the case of the latter process, the molds are typically made from transparent plastic hence allowing consumers to perceive the excellent transparency.

6.4. Milling/Extrusion-Forming. The most common process for the production of bar soaps is the milled bar process. The process has two separate stages, a drying stage followed by a finishing stage. Typical production rates on high-speed lines achieve the order of 400 bars/min. The limiting step in this is usually the bar-stamping rate, which has been the subject of many technological advances in recent times.

During the drying stage, the wet base soap containing ca 30% water is pumped into a mixing vessel (crutcher) where the addition and blending of other additives may be achieved. Minor ingredients include excess fatty acids and preservatives. Higher levels of additives may also be added at this stage including fatty acids for super-fatting, and synthetic surfactants. Alternatively any of these additives and especially those which are either heat sensitive or are liable to phase separate in the crutcher can be injected into the soap stream prior to the main soap drier. The commonest type of soap drier utilized is a vacuum design. The neat soap from the crutcher at ca 90°C, is first heated to around 130°C in one or more low pressure heat exchangers, and then sprayed onto the walls of an evacuated tower using a nozzle. The nozzle can either be unidirectional, mounted on a rotating shaft, or statically mounted and multidirectional. Cooling and drying is achieved in one step through the flash release of moisture as vapor, which occurs upon introduction of the pressurized superheated soap into the vacuum chamber. The dried, cooled soap is scraped off the tower wall with a scraper blade mounted on a rotating shaft. The moisture in the dried soap is dependent on the flow rate, the temperature of the soap, and the pressure in the vacuum chamber; the last also controls the final temperature of the soap. The dried soap is obtained at the bottom of the tower in the form of small chips through an airlock created by screw extrusion of the soap through a multi-holed orifice plate.

Alternative soap drying operations occasionally used include atmospheric flash drying and chilled surface drying. In the case of atmospheric flash drying the superheated soap (~190–220°C) is sprayed at pressures of about 2.8 MPa (400 psi) (with specially designed nozzles) as small particles into the upper part of a tower (at atmospheric pressures). The spraying process causes a rapid loss of moisture from the superheated soap in the form of steam. Cooling of the hot, dry soap particles is achieved using cooling air which is blown into the bottom of the tower. The air cools the soap as it falls to the bottom of the tower. The cooling air is usually humidified to prevent overdrying of the soap. The soap is removed from the bottom of the tower. The chilled surface drying process is similar to atmospheric drying, with the cooling process being driven by a chilled surface as opposed to air flow through a tall tower. The wet soap is superheated in high pressure, nonboiling heat exchangers. Drying is achieved by the release of steam when this superheated soap is introduced into a chamber with a slight negative pressure, which is commonly referred to as a flash chamber. The resulting hot, dry soap melt is cooled through the formation of a thin film on a chilled surfaced, commonly in the form of a roll (rotating cylinder). The hot dry soap falls into the small gap (~10–50 μm) formed at the interface between a large chilled roll and a smaller, temperature- controlled (may be heated or cooled) applicator roll that aids in uniform film formation. As the chilled roll rotates, the dry, cold soap is removed via scraping with a doctor blade and emerges in the form of flat flakes. The amount of soap drying is governed by the temperature at which the soap is introduced and the air flow in the flash chamber. This process is exceptionally good for modern synthetic surfactant containing formulations because it is amenable to stickier in-process materials. This drying approach can also be achieved using a chilled belt in place of the chilled roll.

For each of these routes the aim is to produce soap chips with moisture content in the range 8–14%.

These dried soap chips are then transferred to the first stage in the finishing line which is usually a low shear ribbon-type mixer. This can be used to incorporate minor ingredients such as pigments, perfumes, dyes, preservatives, and antibacterial actives. This stage can also be used to roughly mix in larger amounts of benefit agents such as polyols, emolient oils, etc although it should be noted that if large amounts of liquid materials are added, a high shear stage will be necessary to fully homogenize these into the soap mass. These additives can be either added manually or in an automated system using weighbelts.

The subsequent stage of the finishing operation is typically a high shear stage. For soap blends which require intensive mixing (eg, translucent soaps) this is usually either a Z-blade or sigma-blade mixer both of which can be thermostatically controlled and sealed to prevent moisture loss. The soap mass from this type of mixer would then be fed into a mill for further processing. For most conventional soaps, a single stage high shear process is used, using a 3-roll mill. In this operation the soap is passed through a series of closely spaced, temperature-controlled steel rolls which dictates product temperature, inputs work into the soap mixture, and provides efficient micromixing. Mills are designed such that successive rolls rotate in opposite directions and at slightly increased rates than the previous roll. Therefore, at the point of contact between two mill rolls, the two surfaces are moving in the same direction but with different speeds. A zone, called a bead, is created at this point of contact where material is micromixed through the high shear nature of the zone. This high shear mixing also causes heating of the product stream. The spacing between the rolls is set to effectively grind gritty particles in the product. At the top roll, the soap is scraped off using a knife blade into ribbons of less than 5 cm in width.

Milling not only provides intimate mixing, but also eliminates variation in ribbon thickness and crushes lumpy materials, eg, overdried soap, which might impact finished bar texture. Milling is also used for the formation of the proper bar soap crystalline phase, which plays a critical role in both the performance properties of the soap bar and the handling characteristics of the in-process soap. For example, too hot a milling temperature can create sticky soap that is difficult to process further, as well as a bar that is mushy in use.

After the high shear stage the soap is transferred directly into an extruder. This extrusion stage commonly referred to as plodding is achieved using two-stage single- or counter rotating twin-worm-screw extruder. The purpose of plodding is to compact the soap noodles into a solid mass of soap which is in a manageable form and devoid of air. The first stage of the plodder pushes the soap through a multi-holed orifice plate which acts as an airlock for the second stage. The second stage is under vacuum to ensure the removal of entrained air which impacts final bar appearance. For difficult to plod and temperature sensitive formulations an intermeshed screw extruder can be used for this second stage of plodding (39). The second stage also pushes the soap through a temperature-controlled barrel which terminates in a cone having a shaped orifice plate. The orifice plate yields a soap plug with proper dimensions for cutting and stamping into the desired bar shape. During this plodding step, heat may be added or removed. The worm screw and conical termination of the barrel force the soap into a plastic mass (at appropriate temperatures), which is welded together and emerges as a smoothly surfaced, continuous plug of soap.

The plug at the exit of the plodder is cut into the appropriate length and directed into the stamping and packaging operations. Product can be stamped into the desired shape on account of its intrinsic plasticity using either fixed capacity or box dies. Capacity dies are a pair of casts pressed together to form the desired shape of the bar. The dies possess a fixed capacity and excess material is pushed outside the mated die pair. The excess, on the order of 20% of the original plug mass, is recycled back to the plodder. Box dies are an arrangement of two dies that, in conjunction with a cavity referred to as a box, form the shape of the bar. The plug is placed into the cavity and the two dies push the soap to fill in the shape confined by the two dies and the box. There is very little excess because this design uses the total mass of material to fill out the shape. However, the resultant bar soap has a band around its perimeter on account of the box. Capacity dies provide greater flexibility in bar shape design, whereas box dies have the advantage of producing much lower amounts of recycle material. Dies are typically produced out of brass, highly polished to produce a high gloss, smooth bar surface, and cooled ($\sim 0-15^\circ$C) to eliminate product sticking during stamping. To further eliminate the sticking of the final bar to the die, liquor of concentrated brine solution or glycerol can be applied to the die surface. This is often necessary with bars containing high liquid fractions such as soap-synthetic surfactant formulations. Alternatives to this low-technology approach to stickiness are either super-chilled dies, or elastomer-coated dies (40). Unfortunately the former can suffer from ice-build up particularly on start-stop operation whereas the latter have no such problems and can be easily tailored to specific formulations.

Stamped bars are then either wrapped or placed in cartons and bundled for sale. The entire bar finishing operation from the plodder to cases of finished product operates at rates of between 150 to 400 bar/min, depending on the stamp design and packaging equipment.

7. Economic Aspects

The world market for soaps and detergents was worth US\$ 88×10^9 in 2000 according to the market research report published by the London School of Hygiene and Tropic Medicine (41). Asia, Western Europe and North America account for about 87% of total industrial soap consumption. Global soap and detergent consumption has grown by 29% in the five years to 2000. The primary engines (drivers) of this sales growth were Western Europe (+31%), Asia (+59%) and Latin America and the Caribbean (+41%). During the same period, the mature North America market expanded by just 14%, while the impact of economic recession has severely curtailed sales in Australasia and the Pacific Rim during the last couple of years. The Middle East and African regions are believed to have expanded sales by some 72% and 65% respectively during the period, from a low base.

The global soap market is dominated by a small number of multinational companies. Soap is only one sector of their product ranges. In multinational companies such as Unilever and Procter and Gamble, soap and detergent ranges typically account for less than 20% of group turnover (in 1999).

Tables 2 and 3 below lists the top 20 companies dominating the global toiletries and cosmetics industry. In terms of value sales, recent acquisitions have slightly altered this pattern.

8. Analytical Methods

8.1. Soap and Related Materials. The two most important reference sources for analytical methods for soap and soap raw materials include the *Official Methods and Recommended Practices of the American Oil Chemists' Society* (42) and the *Annual Book of ASTM Standards of the American Society for Testing and Materials*, Volume 15.04 (43).

The main characteristics of soap are as following:

1. Anhydrous soap content: a soap sample dissolved in a mixed solvent of ethanol and water is treated with mineral acids. The liberated fatty acid reacts with sodium hydroxide solution to form soap. The resulting soap is dried and weighed to establish the anhydrous soap content of the original sample.
2. Total fatty acid and real soap content: fatty acids are librated from a sample with mineral acid and are subsequently recovered by a series of petroleum ether extractions, dried and weighed. The total fatty acid content is the weight fraction of the fatty acids in the sample. The real soap content can be derived by multiplying the percent total fatty acid by gravimetric factor for the type of soap.
3. Moisture content of soap: the main method used to measure the moisture content is the Karl Fischer titration. It is a rapid method and is especially useful when water is present in small quantities. Another method is the oven drying at 105°C as described in AOCS Method Da 2a-48 and by ASTM method D460 Section 14 (42,43).
4. Free glycerol content of soap: this method determines the free glycerol content of soap by way of oxidation of the glycerol with periodic acid.

5. Free fatty acid and free alkalinity in soap: these are determined by titration, with standard alkali or acid as appropriate, to the phenolphthalein end point.

Gas chromatography and high performance liquid chromatography are two instrumental analytical methods widely used to determine the free fatty acid composition, glycerol content and minor ingredients.

8.2. Evaluation Methods for Finished Bars. The color of soap bars is evaluated by visual comparison of fresh product against various standards such as paper or plastic color chips and retained standard product samples. Another method is measuring the reflectance color of a sample using an instrument.

Other bar properties are evaluated either by washing performance or by instrumental methods. These include lather volume, bar mush, dry cracking, wet cracking, bar feel during washdown, bar hardness and foreign particulate matter in soap. The details of these measurements are illustrated in the reference 44.

9. Health and Safety Factors

The manufacture of soap poses some material handling concerns because of the reaction of strong caustics with either neutral fats and oils or fatty acids at relatively high temperatures. The caustics, ie, sodium hydroxide and potassium hydroxide, represent the primary hazard. At around 50% concentrations, these caustics are extremely corrosive and may cause serious body burns and eye injuries if not removed quickly through rinsing with copious amounts of water. Appropriate protective clothing is strongly urged when handling these materials.

Soap as used in personal cleansing products has a long safe history of use. Modern soaps have been specifically formulated to be compatible with skin and to be used on a daily basis with minimal side effects. However excessive use of soap for skin cleansing can disrupt the natural barrier function of skin through the removal of skin oils and disruption of the lipid bilayer in skin. This can result in imperfect desquamation or a dry appearance to skin and cause an irritation response or erythema, ie, reddening of the skin. Neither of these is a permanent response; and the elicitation of this type of skin reaction depends on the individual's skin type, the product formulation, and the frequency of use.

There is a considerable amount of research into the compatibility of cleansing products with skin (22,45). Modern soap manufacturers improve the skin compatibility of their products through a variety of chemical testing methods. These methods are often used to evaluate the mildness (irritation potential) of test formulations in comparison to other formulations on the basis of the dry skin and irritated (red) appearance of skin. There are many reports of comparative studies of various formulations and their mildness-to-skin; however, the results of these overly exaggerated test methods may not reflect consumer experience with products (22). Upon direct contact with other sensitive membranes such as eyes, soap may also cause irritation in the form of stinging. Again, this is a temporary response which can be rectified through rinsing with water. Ingestion of soap poses little risk at the levels of materials usually ingested. Typically, temporary minor irritation of mucous membranes and gastrointestinal disorders, eg, nausea, vomiting, and diarrhoea, may be experienced.

9.1. Hygienic and Social Benefits. Poor sanitation, bad personal hygiene and communicable diseases have caused more misery and deaths in history, than any war or conflict. Long before the role of micro-organisms in causing disease was established, Dr. John Snow (1813–1858) through brilliantly insightful but painstaking work, clearly proved the existence of a link between the dreadful London cholera epidemics in the 19th century, and poor sanitation conditions (46). His work also demonstrated the importance of focusing on “mode of communication” for controlling spread of disease. Around the same period, Sir Edwin Chadwick (1800–1890) also promoted the radical thought of proactive social control of diseases, by dealing with their causes and preventing their spread. He vehemently advocated the use of water and soap for cleanliness as a means of disease control (47). The rising awareness regarding importance of cleanliness, personal hygiene and the role of soap in achieving it, lead to abolition of duty on soap in 1852 in Great Britain, at an annual loss of GBP 1,126,000 in tax revenue (48). The soap consumption in Great Britain doubled in the subsequent 30 years, to reach nearly 7 kg per year per person. Improvement in personal hygiene, more frequent and more effective cleaning of clothes, and development of convenient products to keep the kitchens, homes, workplaces etc clean, made significant contribution to control of communicable diseases, during this era.

However, even today, more than two million children die every year, owing to unhygienic habits and habitats, from diarrhoeal diseases (49). The list of other rampantly prevalent communicable diseases includes viral hepatitis, salmonellosis, typhoid, trachoma, ringworm, etc. Contaminated hands, clothes, dishes, dishcloths, etc serve as vectors transmitting pathogens to foodstuff and susceptible hosts, causing the spread of such diseases. Appropriate use of soaps and surfactants for improving overall cleanliness would be an effective intervention for prevention, as opposed to treatment, of these infection diseases. Soap does not necessarily kill germs, but helps to wash them away by improving wettability, reducing their numbers to below the critical infectious dose. Several recent research studies (49–51), for example, have shown that simple promotion of hand washing with soap can reduce the incidence of pneumonia and diarrhoea by more than 40%, among people living in poor conditions. Such measures could avert more than one million diarrhoeal deaths of children annually, in developing countries. Many international agencies such as UNICFF / World Bank, Governments, and Private Sector Companies are joining hands to promote this campaign. For example, Unilever South Africa and Department of Water Affairs and Forestry (DWAF) of South Africa have jointly launched in 2003, a major campaign to teach school children that a simple act of washing hands with water and soap can save many lives (52). The initiative is likely to become a major lifesaving movement in the years to come, in several developing countries.

10. Principal Uses

The earliest discovered use of soap, as a personal or fabric or utensil cleansing or detergency agent, still continues to be the most dominant application of all soaps, ie, salts of fatty acids. Of the soap produced in 1987 (5.4×10^5 metric tons), approximately 80% was for use in bar soap (53). The soaps used in the soap bar are usually a mixture of different chain lengths, saturated and unsaturated fatty acid salts of sodium, potassium, and triethanolamine. The short chain soaps, $<C_{12}$, and unsaturated long chain soaps, are soluble in water at room/warm temperature therefore they are capable of generating foam during washing. Longer chain fatty acid soaps are less soluble in water than the shorter ones and play a role in structuring the soap bar and contribute to the mechanical strength of the bar. A typical mass-market toilet soap bar formulation contains ca 85% soap, ca 12% water and minor ingredients such as glycerol, preservatives, salt, colorants and perfumes.

In skin care products fatty acids are usually partially neutralized with alkaline or amine bases to create a mixture of soap and fatty acid which build a surfactant network to thicken the aqueous phase and also emulsify the oil droplets. The long chain fatty acids deployed for this purpose are normally a mixture of palmitic and stearic acid. A simple formulation for a vanishing skin cream contains about 20% of fatty acid and its potassium soap mixture and 80% water. Cetyl alcohol, glycol monostearate and glycerol monostearate are common co-surfactants incorporated inside the network.

Over the centuries soaps have found many diverse applications by virtue of their interesting physico-chemical characteristics. The amine and alkali metal soaps are fairly soluble in water, and as surface active agents they are important ingredients of many industrial cleansing or defatting preparations deployed in textile processing, wool and leather processing, electroplating of metals, etc. Their surface activity is also put to use for preparing or stabilizing emulsions such as water-based paints, insecticide sprays, polymer and rubber latexes, pharmaceutical suspensions, cosmetics and personal care creams etc. They are used as foaming or lathering agents in shaving creams, fire fighting preparations, tooth pastes, low density concrete etc (54). The surface tension lowering property of soaps is also exploited for noninsecticidal control of insects, because either insects or their larvae cannot float on water once its surface tension is lowered. Owing to the amphiphilicity of their molecules many soaps self-assemble in interesting planar or fibrous liquid crystalline or crystalline forms, both in aqueous and non aqueous media. They have an ability to entrap and immobilise a large proportion of the solvent media, within three-dimensional frame-work structures. This property is used, eg, in the preparation of anti-perspirant or deodorant sticks using sodium stearate (55); or in the preparation of lubricating greases using lithium/sodium/calcium/aluminium stearates, or hydroxy stearates (56).

As soaps are good wetting agents they provide good adhesion for preparing multiphase composite structures. For example, asphalt cement does not ordinarily bond well with stone aggregates in the presence of moisture or water. Soaps enhance this bonding, making asphalted roads more water resistant (57). The dry metal soaps such as magnesium or calcium stearates are excellent solid phase lubricants in processing of solids. They are used for achieving good die and punch release, in pharmaceutical tableting (58), or for facilitating metal forming operations such as wire drawing, sheet rolling etc (59). Calcium stearate has been recommended as bread-dough strength improver and crumb softener (60,61). Some soaps such as zinc-undecylenate, are also deployed for germ-inhibition or antifungal action (62).

BIBLIOGRAPHY

"Soap" in *ECT* 1st ed., Vol. 12, pp. 553–598, by G. W. Busby, Lever Brothers Co.; in *ECT* 2nd ed., Vol. 18, pp. 415–432, by F. V. Ryer, Lever Brothers Co., Inc.; in *ECT* 3rd ed., Vol. 21, pp. 162–181, by F. S. Osmer, Lever Brothers Co., Inc.; in *ECT* 4th ed., Vol. 22, pp. 297–326, by R. G. Bartolo and M. L. Lynch, The Proctor & Gamble Co.; "Soap" in *ECT* (online), posting date: December 4, 2000, by R. G. Bartolo and M. L. Lynch, The Proctor & Gamble Co.

CITED PUBLICATIONS

1. J. Davidson, E. J. Better, and A. Davidson, *Soap Manufacture*, Vol. 1, Interscience, New York, 1953.
2. L. Spitz, ed., *Soap Technology for the 1990's*, American Oil Chemists' Society, Champaign, Ill., 1990.
3. E. Woollatt, *The Manufacture of Soaps, Other Detergents and Glycerine*, John Wiley & Sons, Inc., New York, 1985.
4. D. Small, ed., *Handbook of Lipid Research 4, The Physical Chemistry of Lipids from Alkanes to Phospholipids*, Plenum Press, New York, 1986.
5. R. G. Laughlin, *The Aqueous Phase Behaviour of Surfactants*, Academic Press, Ltd., London, 1994.
6. T. Warnheim and A. Jonsson, *Progress Coll. Polym. Sci.* **88**, 18 (1992).
7. T. Warnheim and A. Jonsson, *J. Coll. Interface Sci.* **138**, 314 (1990).
8. S. Zhu and co-workers, "Interaction of Acid Soap of Triethanolamine Stearate and Stearic Acid with Water", paper submitted to Longmuir, 2006.
9. P. Ekwall and L. Mandell, *Kolloid Z.* **233**, 938–944 (1969).
10. P. Ekwall, L. Mandell, and K. Fontell, *J. Coll. Interfacial Sci.* **28**, 219–226 (1968).
11. P. Ekwall, *Coll. Polym. Sci.* **266**, 279–282 (1988).
12. P. Ekwall and Fontell, *K. Coll. Polym. Sci.* **266**, 184–191 (1988).
13. S. Zhu, M. Heppenstall-Butler, M. Butler, P. D. A. Pudney, and D. Ferdinando, *J. Phys. Chem. B* **109**, 11753–11761 (2005).
14. D. Chapman, *The Structure of Lipids by Spectroscopic and X-ray Techniques*, John Wiley & Sons, Inc., New York, 1965.
15. S. Zhu and R. Peschar, "Structure Determination of Triethanolamine Stearate by X-ray Diffraction" paper in preparation.
16. M. J. Burger, L. B. Smith, F. V. Ryer, and J. E. Spike, *Proc. Nat. Acad. Sci.* **31**, 226 (1945).
17. R. H. Ferguson, Oil Soap 6 (Jan. 1944).
18. GB Pat. 2,181,739 (A) (Apr. 1987), P. Eymond and A. Hight (to Unilever).
19. R. Wolf, *Dermatology* **189**, 217 (1994).

20. K. D. Ertel, B. H. Keswick, and P. B. Bryant, *J. Soc. Cos. Chem.* **46**, 67 (1995).
21. B. H. Keswick, K. D. Ertel, and M. O. Visscher, *J. Soc. Cos. Chem.* **43**, 187 (1992).
22. C. Prottey, P. J. Hartop, and T. F. M. Ferguson, *J. Soc. Cosmet. Chem.* **24**, 473–492 (1972).
23. EP 0090644 B1 (Oct. 1983), A. T. Clark, R. B. Edwards, and G. N. Irving (to Unilever).
24. R. M. Dahlgren, M. F. Lukacovic, S. E. Michaels, and M. O. Visscher, in A. R. Baldwin, ed., *Proceedings of the Second World Conference on Detergents*, American Oil Chemists' Society, Champaign, Ill., 1987.
25. H. W. S. Chan, *Autoxidation of Unsaturated Lipids*, Academic Press, Inc., Orlando, Fla., 1987.
26. U.S. Pat. 4,151,105 (Apr. 1979), J. R. O'Roark (to Hewitt Soap Co., Inc.).
27. U.S. Pat. 5,387,362 (Feb. 1995), F. R. Tollens, P. J. Kefauver, and S. W. Syfert (to Procter & Gamble Co.); U.S. Pat. 5,264,144 (Nov. 1993).
28. N. M. Moroney and co-workers (to Procter & Gamble Co.).
29. U.S. Pat. 5,296,159 (Mar. 1994), D. B. Wilson and co-workers (to Procter & Gamble Co.).
30. EP 0537964 B1 (Apr. 1993), J. G. Chambers and G. Iriam (to Unilever), EP 0699234 A1 (Nov. 1994), J. G. Chambers and G. Iriam (to Unilever), U.S. Pat. 5,264,145 A (Nov. 1993), D. French and co-workers (to Procter & Gamble), U.S. Pat. 5,620,951 A (Apr. 1997), R. Subramanyam and B. Gu (to Colgate).
31. EP 0,472,320,A1 (Feb. 26, 1991), J. F. Ashley, A. C. Coxon, and R. S. Lee (to Unilever).
32. U.S. Pat. 4,954,282 (Sept. 1990), K. J. Rys, A. P. Greene, F. S. Osmer, and J. J. Podgorsky (to Lever Brothers Co.).
33. M. B. Finkey, N. C. Corbin, L. B. Aust, R. Aly, and H. I. Maibach, *J. Soc. Cosmet. Chem.* **35**, 351 (1984).
34. EP 0090649 B1 (May 1983), A. T. Clarke, R. B. Edwards, and N. G. Irving (to Unilever).
35. EP 350306 (June 1986), J. G. Chambers and T. Instone (to Unilever), EP 385796 (Jan. 1990), J. G. Chambers, T. Instone, and B. S. Joy (to Unilever), WO 9209679 (June 1992), M. Kacher, J. Taneri, J. Camden, P. Vest, and S. Bowles (to Procter & Gamble), WO 9604360, (Feb. 1996) B. Wiegand, A. Figueroa, Brunsman, and A. Zyngier (to Procter & Gamble), WO 9526710 (Oct. 1995), M. Kacher and co-workers (to Procter & Gamble), U.S. Pat. 4,584,126 A (Apr. 1986), D. P. Joshi (to Colgate), EP 1478725 A1 (Sept. 2000), A. Sachdev (to Colgate).
36. EP 0530156 A2 (Mar. 1993), B. Roberto, M. Luciano, and S. Sergio (to Colgate).
37. V. World Pat. 9532705 (Dec. 1995), M. Fujiwara, C. Vincent, K. Villa Anathapadmanabhan, and V. Virgilio (to Unilever).
38. U.S. Pat. 4,758,370 (July 1988), E. Jungerman, T. Hassapis, R. A. Scott, and M. S. Wortzman (to Neutrogena Corp.).
39. U.S. Pat. 5,534,212 (1996), K. D. Chokappa and V. M. Naik (to Unilever).
40. EP 0276971 A2 (Aug. 1988), M. Adams and B. Edmondson (to Unilever); EP 0766730 B1 (Jan. 1996), M. Adams and co-workers (to Unilever).
41. *The Global Market for Soap*, by London School of Hygiene and Tropic Medicine, http://www.globalhandwashing.org/Publications/MarketStudy.h
42. R. C. Walker, ed., *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th ed., American Oil Chemists' Society, Champaign, Ill., 1994.
43. *Annual Book of ASTM Standards*, Vol. 15.04, American Society for Testing and Materials, Philadelphia, Penn., 1994.
44. T. E. Wood, in L. Spize, ed., *Soaps and Detergents, A Theoretical and Practical Review*, AOCS press, Champaign, Ill., 1996.

45. F. R. Bettley and E. Donoghue, *Brit. J. Derm.* **72**, 67 (1960); D. D. Strube and G. Nicoll, *Cutis* **39**, 544 (1987).
46. N. Paneth, *Epidemiology* **15**, 514–516 (2004).
47. S. E. Finer, The Life and Times of Sir Edwin Chadwick, Barnes & Noble, 1970.
48. A. Campbell, *Chemistry in Britain* **34**, 56 (1998).
49. S. P. Luby, M. Agboatwalla, J. Painter, A. Altaf, W. L. Billhimer, and R. M. Hoekstra, *JAMA* **291**, 2547 (2004).
50. V. Curtis and S. Cairncross, *The Lancet-Infection Diseases* **3**, 275 (2003).
51. S. P. Lubey, M. Agbotwalla, D. R. Feikin, J. Painter, W. Billhimer, A. Altaf, and R. M. Hoekstra, *Lancet* **366**, 225 (2005). www.thelancelet.com.
52. DWAF, South Africa, Media Release, 16th Oct. 2003.
53. *1987 Census of Manufacturers*, Vol. II, U.S. Government Printing Office, Washington, D.C., Product Statistics, Table 6A; S. Colwell, *Soap Cos. Chem. Spec.* **71**, 32 (1995).
54. U.S. Pat. 5,326,556 (1994), A. G. Barnet and M. R. Mezikofsky (to Gillete Co.).
55. U.S. Pat. 5,232,689 (1993), D. E. Katsoulis and J. M. Smith (to Dow Corning Corp.); U.S. Pat. 5,424,070 (1995), R. B. Kasat and B. D. Moghe (to Mennen Co.).
56. A. C. Witte, “Grease Manufacture”, in J. J. McKetta, ed., *Encyclopedia of Chemical Processing and Design*, Vol. 25, Marcel Dekker, New York, 1987.
57. *Introduction to Asphalt*, Manual series No. 5, The Asphalt Institute, Maryland, U.S. 1965; B. R. Mogul, “Asphalt Emulsion”, in J. J. McKetta, ed., *Encyclopedia of Chemical Processing and Design*, Vol. 14, Marcel Dekker, 1977.
58. G. K. Bolhuis and A. W. Holzer, “Lubricant sensitivity”, in G. Alderborn and C. Nystrom, eds., *Pharmaceutical Powder Compaction Technology*, Marcel Dekker, New York, 1996.
59. F. Delamare and P. Montmitonnet, “Metal Soap Lubrication in Metal Forming”, in *Proc. Conf. FORMULA (Nice 1987)*, Societe Fransçaise de Chimie.
60. D. K. Dubois, *Dough Strengtheners and Crumb Softeners II-Products, Types, and Functions*, American Institute of Baking, Technical Bulletin, Vol. 1, Issue 6, 1979.
61. B. S. Kamel, *Surfactants in Baking Foods*, American Institute of Baking, Technical Bulletin, Vol. 15, Issue 7, 1993.
62. Merck Index, 13th ed., 2001.

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Table 1. **Typical Fatty Acid Chain Length Distributions for Oils and Fats Used in Soap-making**[a]

Chain length	Trivial name	Coconut	Palm Kernel oil	Babassu	Tallow-UK	Tallow-Brazil	Palm oil	Palm stearine	Palm stearine	Lard	Soya bean oil	Sunflower seed oil	Rice bran oil
<C10		9.5	3.4	5.0	0	0	0	0	0	0	0	0	0
C10	capric	6.0	3.0	6.0	0	0	0	0	0	0	0	0	0
C12	lauric	47.0	47.0	44.0	0	0	0	0	0	0	0.1	0	0.1
C14	myristic	18.0	16.2	17.4	3.0	3.8	1.3	1.4	1.5	1.6	0.2	0	0.6
C16	palmitic	9.5	8.6	7.8	25.4	26.2	42.9	57.5	70.4	23.0	11.0	3.5	23.5
C18	stearic	2.1	2.1	1.8	20.9	28.9	4.8	5.2	5.4	10.3	4.4	2.9	3.0
C20	arachidic	0	0	0	1.0	0.1	0.2	0.1	0	0.2	0.6	0.4	0.7
>C20		0	0	0	0.8	0.2	0.2	0.1	0	0.1	0.6	0.6	0.7
<C18:1		0.1	0.2	0.2	4.5	5.2	0.5	0.3	0.3	4.4	0.5	0.5	0.4
C18:1	oleic	5.6	15.9	15.9	39.1	33.7	38.9	28.4	18.1	48.3	23.8	33.5	34.8
C18:2	linoleic	2.6	2.9	1.9	4.7	1.5	10.6	6.7	4.3	9.3	51.0	58.6	34.6
C18:3	linolenic	0	0	0	0.3	0.2	0.1	0.1	0	0.8	7.8	0	0.7
C20:1	gadoleic	0	0	0	0.2	0.2	0.2	0	0	0.9	0	0	1.0
>C20:U		0	0	0	0.1	0	0.3	0	0	1.2	0	0	0
Iodine value		10	19.5	17.7	48.2	38.0	54.6	38	24	67.5	133	135	95.7

[a] Key: All analyses ex Unilever.

Codes: C18:1 – cis-isomer of monounsaturate
C18:2 – cis-cis-disomer of diunsaturate
C18:3 – cis-cis-cis-trisomer of triunsaturate
>C20:U – all unsaturated chainlengths >20 carbon atoms

Table 2. **The Top 20 Global Companies in the Soap and Toiletries Market**[a]

Position	Company	% Value of world
1	Unilever	10.07
2	Procter & Gamble	7.41
3	Gillette Group	7.66
4	Colgate Palmolive	4.5
5	Johnson & Johnson	4.45
6	Shiseido	4.32
7	Estee Lauder	4.21
8	Revlon	3.42
9	Wella	2.27
10	Henkel	2.13
11	Kanebo	2.13
12	LVMH	1.94
13	Avon Products	1.91
14	Kao	1.88
15	Reckitt-Benckiser	1.88
16	Beiersdorf	1.56
17	Amway	1.55
18	Mary Kay	1.54
19	Coty	1.49
20	Lion 1.07	1.07

[a] Source: Euromonitor, 2000.

Table 3. **Key Companies: Brand Ownership in Top 50 Brands**[a]

Name of company	Brands in the top 50	Brand and position
Unilever	12	Lux (10), Rexona (25), Dove (25), Ponds (16), Lifebuoy (44)
Procter & Gamble	8	Crest (20), Camay (50)
Colgate-Palmolive	3	Palmolive (18)

[a] Source: Market Assessment Publications, 1999.

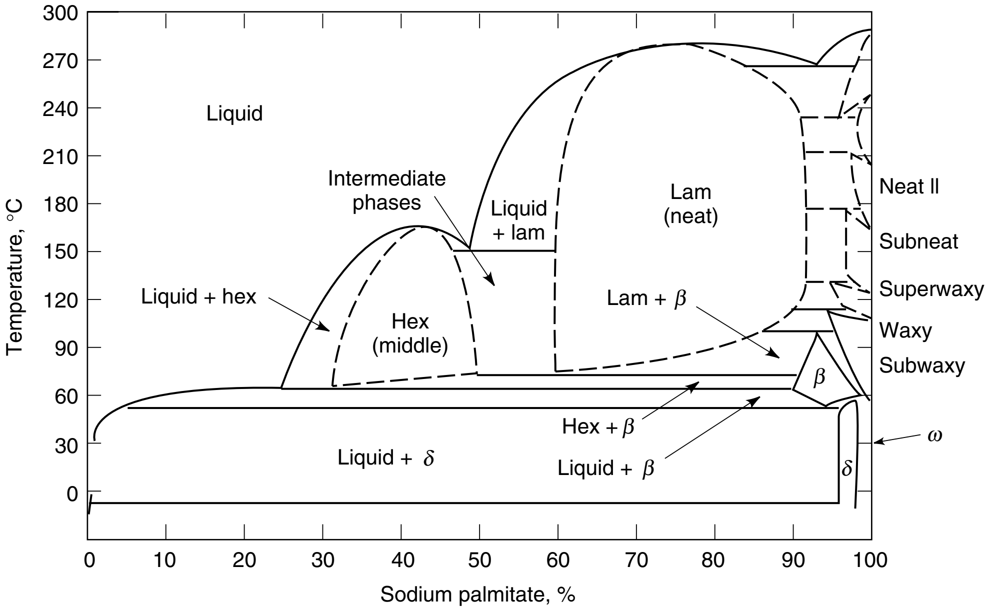

Fig. 1. Binary soap–water phase diagram for sodium palmitate (5). Courtesy of Academic Press, Ltd.

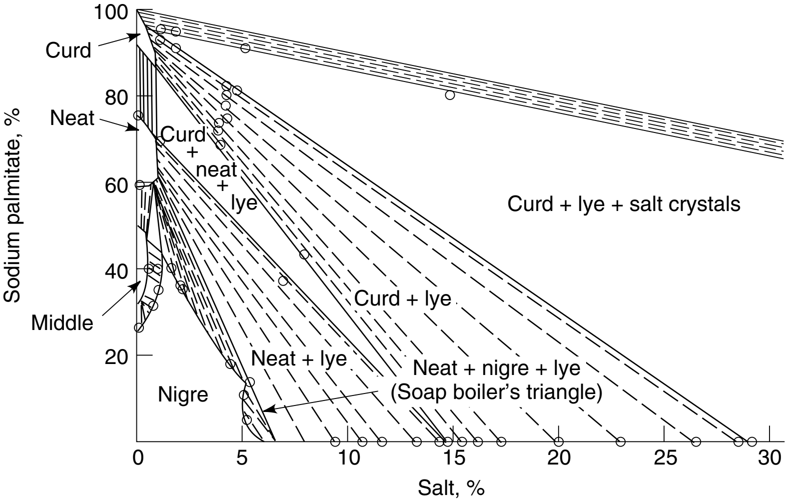

Fig. 2. Ternary soap–NaCl–water phase diagram for sodium palmitate (5). Courtesy of Academic Press, Ltd.

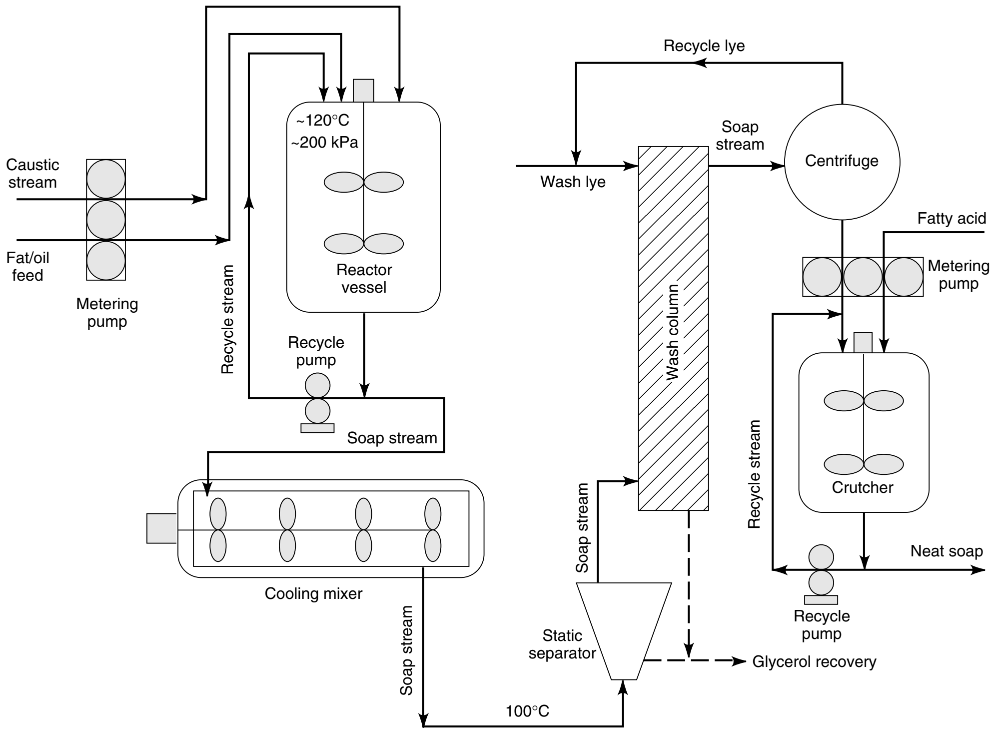

Fig. 3. Process stream diagram for a continuous saponification soap manufacturing facility. To convert kPa to psi, multiply by 0.145.

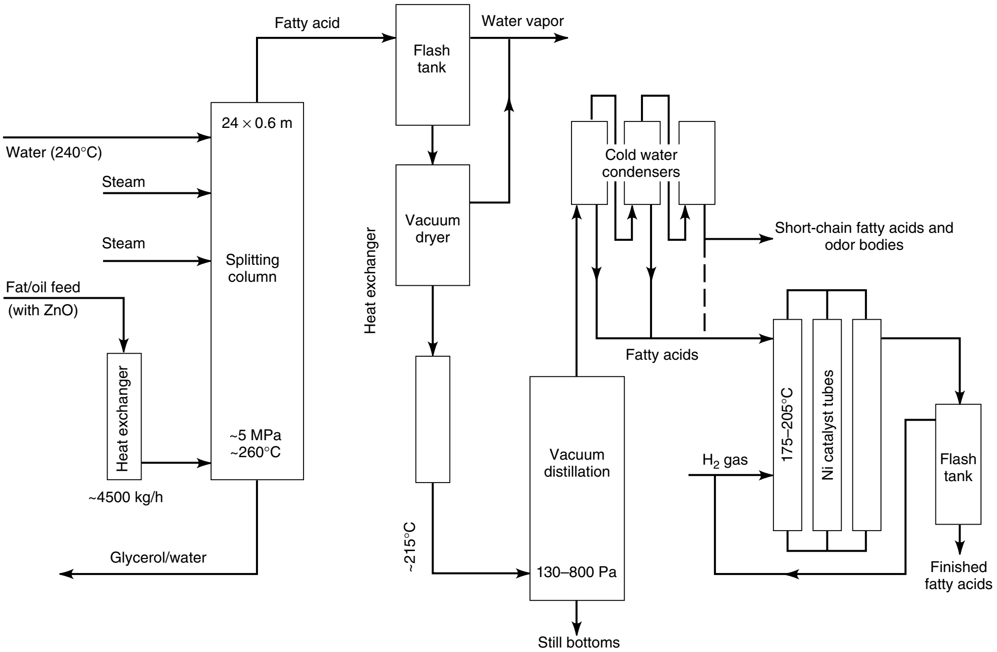

Fig. 4. Process stream diagram for the production of fatty acids through hydrolysis of fats and oils. Steam is at 5.2–6.2 MPa (750–900 psi). To convert MPa to psi, multiply by 145. To convert Pa to mm Hg, multiply by 0.0075.