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Soap and Fat-Based Detergents

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ABSTRACT

Many materials made from fats and oils derive their importance from their ability to modify the surface behavior of the liquid in which they are dissolved. These compounds are grouped under the broad classification of surface active agents or surfactants. Depending on their use, they are classified as detergents, wetting agents, emulsifiers, dispersing agents, etc. The oldest, and still one of the most important surfactants, is ordinary soap; twenty-three percent of all the tallow produced in the United States goes into soap. This paper covers the present state of the art of soap technology, and the most important classes of fat-based surfactants.

TOILET SOAPS

Soap is the oldest known surface active agent with a long history of acceptability. It is especially useful in toilet bars and in applications where soft water detergency is required. It has, however, two disadvantages: poor performance in hard water due to precipitation of insoluble calcium and magnesium soaps, and instability on the acid side. Soap was the only important surface active agent until the first half of the 20th century. Wartime fat shortages during World War I and World War II stimulated the search for substitutes. This gave rise to the development of synthetic detergents based either on fats or petrochemicals. During the last thirty years, synthetic surfactants have gradually replaced soap in most cleaning applications, except bar soaps, where fatty acid soaps still are the major factor today.

The basic reaction of soap making consists of heating fats with an alkali to yield soap and glycerine. While this seems simple, the technology of soap making is involved and borders on an art due to the extraordinary complex physical nature of soap and its aqueous systems. After saponification, soap passes through a series of phase changes, followed by removal of impurities, the recovery of glycerine, and the reduction of the moisture to relatively low levels. The complete series of operations in the production of a "settled" soap kettle is: (a.) reaction of fat with alkali until it is largely saponified; (b.) graining the soap from solution with salt and recovery of the glycerine; (c.) boiling with excess alkali to complete saponification; (d.) separation of the batch into two immiscible phases: neat soap and "niger." This is the "fitting" operation.

The successive operations to produce a straight kettle soap are called changes. The traditional soap-boiling process is done in huge kettles, often four stories high with capacities of 80,000 to 100,000 lbs. Saponification and the various changes take between five and seven days. These traditional soap-boiling procedures, though they seem old fashioned, are still used widely all over the world today, though at a declining rate.

The reasons for this decline are twofold. First, since the early 1950s, there occurred the rapid replacement of soap by synthetic detergents in most laundry products. Second, during World War II many European soap plants were destroyed and had to be replaced. This encouraged the development of new, more efficient continuous processes to replace the old kettle-boiling process. European firms, particularly in Italy, Sweden, and Germany, developed a number of new, often ingenious processes that have become the method of choice whenever new soap plants are built today.

Continuous processes fall into two categories. First, there are processes based on the continuous saponification of fats. Most important of these are the DeLaval, Sharples, Mechaniche Moderne, and the Mazzoni processes. The second group is based on the continuous splitting of fats into fatty acids, followed by distillation and neutralization of the fatty acids. The most important examples in this category are the Mills, the Mazzoni SB, and the Armour processes.

Sharples Process

Steps in the Sharples continuous process are based on the traditional kettle soap process, i.e., saponification, washing, fitting. At each step high speed centrifuges are used to achieve rapid and continuous saponification of (a) soap and lye, and (b) neat soap and nigers. The time required to convert the feed stock to neat soap is less than 2 hr. Fresh fat is mixed with wash lye with a high glycerine content. This wash lye has come up through several stages of the process in the presence of recycling masses of already saponified materials. The neat soap from the Sharples process is light and clean, since the fat is heated only for one or two min before saponification. Saponification is rapid, and the soap is clarified four times under a high centrifugal force. The use of automatic flow control and interlocking proportioning pumps accurately controls the entire process. Standard plants have capacities up to 13,000 lb./hr.

DeLaval Process

In this process developed in Sweden, continuous saponification is achieved in a technique similar to the Sharples process. The DeLaval process is a centrifugal process characterized by a hermetically enclosed system with automatic control of the washing and fitting operation. The speed of fat and caustic addition is controlled automatically by a unique viscosity sensing device. The viscosity of soap mass decreases rapidly to a minimum as the lye concentration goes down to ca. 0.15% NaOH and increases rapidly again as the alkali content increases. The device utilizes the fact that at a salt content of ca. 1%, the soap mass exhibits minimum viscosity. The amount of NaOH in a saponified soap and the amount of sodium chloride in the finished soap are controlled by choosing the proper viscosity setting on the control instrument.

Mazzoni and Monsavon Processes

These two processes employ an interesting feature: a proportioning pump which consists of 8 pumps driven by the same motor. Each pump is capable of individual adjustments to balance the stream of one component with the seven other streams.

Continuous Fatty Acid-Based Soap Manufacturing

The second approach to modern continuous soap manufacturing is the fatty acid route. The first process of this type was introduced by Procter and Gamble and is based on a number of patents issued to Mills. It involves, as the first step, splitting the fat to produce fatty acids. The acids are then distilled. The fats, usually tallow and coconut oil, are blended in the desired ratio and mixed with a small amount of powdered zinc oxide. The zinc oxide is a catalyst for the splitting operation. The fatty acids, cooled to 82 C, are fed continuously with caustic solution via a proportioning pump to a high speed mixer where saponification takes place almost instantaneously. The strength of the caustic is so adjusted that the composition of the product conforms to the range of ordinary neat soap; sufficient salt is added to yield a soap with the customary electrolyte level. Touch-up hydrogenation is sometimes used in order to improve the quality and stability of the fat stock used. Potassium soaps of high purity can be prepared as readily as sodium soaps. High grade toilet soaps equal in quality to those made by the best kettle soap process are made by the Mills process.

Mazzoni introduced a fatty acid neutralization process using either sodium hydroxide (SC process) or sodium carbonate (SCT process). Distilled fatty acids and caustic soda flow to a preheater and are heated to ca. 60 C. They are then fed to a proportioning unit. The proportioning unit consists of two duplex pumps driven by the same motor, but with variable speed adjustments to accomodate output requirements. The stroke length can be adjusted to deliver a stoichiometric balance between the reactants. The circulating soap mass passes through a chamber equipped with a pH electrode. The signal from the electrode is transmitted to the control unit which maintains a constant pH by causing the stroke length of one of the caustic pumps to be adjusted according to the pH signal received.

The Armour process represents another variation of a continuous fat splitting, distillation, and neutralization procedure. It differs in several important points from the Mills process. The tallow and coconut oil are not premixed, but are separately split and distilled. The plant utilizes two Colgate-Emery fat splitters; splitting is done without a catalyst. The splitters have an hourly rate of ca. 10,000 lb. The fatty acids are distilled using a semifractionating type unit, similar to a traditional fractionating still, but with fewer theoretical plates. An odor cut is removed to improve the quality of the soap. The distilled fatty acids are mixed to give the appropriate tallow/coco ratio and then are neutralized using a DeLaval unit. These are similar to the units described for the saponification of neutral fats and are based on viscosity differentials. While very efficient for the specific neutralization reaction occurring when fatty acids react with sodium hydroxide in the presence of small amounts of salt, the great sensitivity of the DeLaval unit decreases formulation flexibility and limits the types of soap that can be manufactured in such a plant. In the final processing step, the neat soap containing 30-35% moisture is heated to 135 C and spray dried in a Mazzoni vacuum dryer. The finishing operation includes all the steps required to convert soap pellets obtained from the drying operation into finished wrapped and cartoned soap bars. The following equipment is needed for these steps: amalgamators, automatic dosing devices for adding solid and liquid additives, preplodders, vacuum plodders, cutters, conditioning tunnels, presses, wrapping and cartoning machines. Different categories of soaps, such as floating, transparent, marbelized, translucent, and hardwater soaps have different processing and equipment requirements. Addition of materials to make either superfatted or hardwater soaps also may require equipment modifications. Superfatted and hardwater soap bars require special surfactant additives which are often fat-based, and this provides a good transition point for a review of fat-based surfactants.

FAT-BASED SURFACTANTS

Surfactants from fats and oils are obtained by making use of the multifunctionality of the fatty acid molecule, which can be modified at three sites: (a) at the terminal carboxyl group; (b) at the alpha carbon atom; (c) at the site of unsaturation. The long carbon chain portion of the fatty acid molecule has an affinity for fatty oils, hydrocarbons, and similar water insoluble, nonpolar compounds; whereas the opposite end of the molecule has an attraction for water. Thus there exists in the same molecule a dual affinity for substances of an entirely different nature. Furthermore, the two ends of the molecule are sufficiently separated for the two affinities, hydrophobic and hydrophilic, to come into simultaneous and independent action. The dual nature of the molecule is an essential condition for surface activity. There must be a proper balance between hydrophobic and hydrophilic properties; if the chain is too long, there will be an imbalance in the direction of too great an affinity for oily materials. This will be shown by limited solubility in water. If the chain is too short, the compound will not be very surface active because of insufficient hydrophobic qualities and lack of colloidal characteristics.

Surfactants are logically and conveniently classified into four categories: anionic, cationic, nonionic, and amphoteric. Anionic surfactants have the fatty hydrophobic chain attached to a hydrophilic negatively charged group, i.e., carboxylate as in the case of soap, or sulfate or sulfonate. Cationic surfactants have the fatty hydrophobic chain attached to a hydrophilic positively charged group, such as ammonium or phosphonium. In nonionic surfactants, the hydrophobic chain is attached to an uncharged hydrophilic group, i.e., polyoxyethylene or polyoxypropylene chains. Amphoteric detergents have the hydrophobic fatty chain attached to a hydrophilic group containing both a positive and a negative charge.

A dramatic industrial development following World War II was the tremendous increase in the production of synthetic detergents for household use. In 1940, 30 million pounds of detergents were produced in the U.S. By 1945 that quantity had increased to 150 million pounds and by 1950 with the advent of heavy duty powders based on synthetic detergents, the volume reached one billion pounds. This rose to two billion in 1955 and to three billion in 1960. At present, this has leveled off at a four billion pound level. In 1975, out of 4.3 billion pounds of surface active agents produced in the U.S., 70%, or about 3 billion pounds, were anionic surfactants; one billion pounds (24%), were nonionic surfactants; 220 million pounds (5.2%), were cationics; amphoterics represented the lowest level, 0.3% or about 15 million pounds.

Anionic Surfactants

The largest group is the anionic surfactants. The most important derivatives in the group are sulfates or sulfonates. Sulfates are compounds where the sulphur is attached to the carbon chain through an oxygen atom, $-C-\overset{|}{\underset{|}{O}}-SO_3^-$. In sulfonates, the sulphur is directly attached to the carbon chain, $-\overset{|}{\underset{|}{C}}-SO_3^-$.

The first, and now only historically important examples, are the sulfated oils. In 1874, castor oil was sulfated and the resultant product was used in the dying of alizarin red, called rouge d′ Adrianople, and led to the name Turkey Red Oil.

The most important group in this category is the alkyl sulfates. These are prepared by reducing fatty acids or fatty esters to fatty alcohol, followed by sulfation and neutralization. Two methods are used for the manufacture of fatty alcohols. High pressure hydrogenation or reduction of the esters with metallic sodium. This subject is covered in greater detail by J. Monick as part of the Short Course.

Several methods are used industrially for the conversion of fatty alcohols to sulfates. Sulfur trioxide is the most basic of the sulfating agents. The use of sulfur trioxide (SO_3) has the advantage of being inexpensive and not requiring excess amounts of sulfating agent. Sulfation with SO_3 results in the formation of only a minimum amount of inorganic salts. On the other hand, being very reactive, more color formation tends to occur with SO_3 than with other sulfating agents. A number of batch and continuous industrial processes have been developed based on the use of sulfur trioxide. Amongst these, the Chemithon process is probably the most important.

Sulfuric acid, i.e., 100% H_2SO_4 or oleum (sulfuric acid supersaturated with SO_3), is also used for the commercial preparation of alkyl sulfates. Both are more convenient than sulfur trioxide, and being liquids at room temperature, can be more readily metered into the reaction system. Sulfation with sulfuric acid or oleum is an equilibrium reaction and excess acid must be used. This requires the removal of spent acid and also leads to salt formation in the finished product. Chlorsulfonic acid continues to be an important agent for the commercial sulfation of fatty alcohols. Ease of handling and the formation of light colored products are some of the advantages of chlorsulfonic acid. The reaction is stoichiometric and is irreversibly driven to completion by the loss of hydrogen chloride. This also represents one of its disadvantages, leading to corrosion problems and the formation of chloride salts in the finished product. Sulfamic acid, NH_2SO_3H, has found some use in commercial sulfation, when preservation of unsaturation or other reactive sites are important. Sulfamic acid provides simultaneous sulfation and neutralization to the ammonium salt.

Sodium alkyl sulfates are stable in alkaline, neutral and weakly acid solutions, but are hydrolyzed by strong acids by an autocatalytic mechanism, since sulphuric acid is formed leading to further hydrolysis. Several salts other than sodium salt are commercially important. The most important are ammonium, potassium and triethanolamine salts. Detergent grade alkyl sulfates have found a multitude of applications. The have been used in synthetic detergent soap bars and the so-called "combo" bars where soap is combined with a synthetic detergent. Because of their excellent detergency, wetting and foaming properties, long chain alkyl sulfates are used widely in liquid products such as shampoos, light duty dishwashing detergents, bubble bath, heavy duty liquids, rug shampoos etc.

Another group is the alkyl ether sulfates. Ethoxylation of long chain alcohol followed by sulfation leads to the formation of these materials. They have properties similar to the corresponding alcohol sulfates. The alcohol ether sulfates may have some nonionic characteristics depending on the length of the intervening oxyethylene group.

Historically, the sulfated monoglycerides represent an interesting group of anionic surfactants. They were introduced in the U.S. by Colgate in the 1940s. They are based on relatively inexpensive raw materials, i.e., one mole of fat, 2 moles of glycerine, and 3 moles of sulphuric acid. The resultant sulfated fatty monoglycerides were at one time used in laundry detergents, toothpaste and shampoos.

Superficially related to the sulfated monoglycerides are the alkylglycerylether sulfonates. This is a class of surface active agents which has received relatively little attention in the literature. Until a recent review by White, references have been limited almost exclusively to patents. This is particularly surprising since alkylglycerylether sulfonates have gained commercial usage in various Procter & Gamble formulations. Alkylglycerylether sulfonates are prepared by reacting a fatty alcohol with ethylchlorhydrin followed by reaction with sodium sulfide in a typical Strecker reaction.

Another group of sulfated detergents are ester and amide sulfonates. These were discussed in detail by A. Cahn as part of the Short Course, and I do not plan to add anything except to indicate that in addition to their use in detergent and "combo" bars, they have recently been used in a newly introduced antidandruff shampoo formulation.

Sulfonated esters and sulfonated amides of carboxylic acids are another group of interesting anionic surfactants. Best known are the sulfosuccinates and the sulfosuccinamates. Aerosol OT (American Cyanamid) is an example of a widely used specialty surfactant with a sulfosuccinate structure. These esters are prepared by the reaction of 2 moles of a fatty alcohol with one mole of maleic anhydride or maleic acid in the presence of an acid catalyst, followed by sulfonation with sodium bisulfite or sodium sulfite.

Alphasulfo fatty acids have received a lot of publicity in recent years, but to date have found only limited commercial application in the U.S.; there has been some activity in Japan and Germany. Alphasulfo fatty acids were first prepared by Gunther in Germany. In this country, they were studied extensively by Stirton and Weil at the USDA's Eastern Regional Laboratories. Alphasulfo fatty acids are prepared by reacting stabilized liquid sulfur trioxide with a fatty acid dissolved in a chlorinated solvent at 15 C. The reaction mixture is then heated to 60 C, cooled and filtered. Neutralization occurs first and completely with the strong sulfonic acid group. The carboxylic acid group is readily esterified by heating the alkylsulfo fatty acid with alcohol; the strong sulfonic acid group acts as a "built-in" catalyst. These products have potential interest as lime soap dispersants in bar soaps and laundry products.

Sulfur-Free Anionic Surfactants

The best examples of nonsulfur-containing anionic surfactants are the acylated amino acids. Fatty derivatives of amino acids and proteins were introduced in the mid-thirties under the trade names Lamepons, Maypons, and Medialons. The first two were prepared by condensing fatty acids with hydrolized proteins derived from leather scraps and other easily hydrolized proteinaceous materials. The Medialons are condensation products of fatty acids and sarcosine (N-methylglycine). Sarcosine is manufactured either by the reaction of methylamine, formaldehyde and hydrogen cyanide, or by the reaction of methylamine with chloracetic acid. The Medialons are then prepared by a typical Schotten-Bauman reaction procedure utilizing the fatty acid chloride and sarcosine. They have been used in shampoos, rug cleaners, and as anti-caries agents in toothpaste under the trade name Gardol.

Cationic Surfactants

Cationic surfactants have at least one hydrophobic group attached directly to a positively charged nitrogen atom. Early in this century, Einhorn and Mannich reported the preparation and antimicrobial activity of certain quaternary ammonium salts, but it was only in the mid-thirties when the commercial potential of these materials was recognized. From this resulted a proliferation of hundreds of products and applications, and cationic surfactants now play an important role as sanitizers, antiseptic agents, germicides, components of cosmetic formulations, textile chemicals, flotation agents, corrosion inhibitors, etc. The U.S. International Trade Commision Report shows that production of cationic surfactants reached over a billion pounds in 1975, representing a 40% increase in volume over 1966.

The general chemistry and properties of these materials are discussed in detail by R.A. Reck and C.W. Glankler as part of this Short Course, and will not be covered further in this section.

Nonionic Surfactants

Most important among the nonionic surfactants are the polyoxyethylene and polyoxypropylene derivatives of fatty alcohols, amides, and acids. Other examples of nonionic surfactant not derived by the addition of ethylene or propylene oxide to a fatty moiety are the glycol, glycerol, and sugar esters, fatty alkanolamides, and anhydrohexitol derivatives. The key to the growth of the nonionic surfactant market to its present level in excess of one billion pounds in the U.S. was the development of commercial processes for the manufacture of ethylene oxide in 1930.

Unlike the anionic and cationic surfactants, the nonionics are not colloidal electrolytes and are incapable of ionization in aqueous solution. Like the other types, they are partially hydrophobic and hydrophilic. The source of the hydrophilicity are functional groups rich in ether oxygen or hydroyl oxygen. These influence the degree of water solubility of the nonionic surfactant, since overall solubility depends on the extent of hydration of this hydrophilic chain. Water molecules are affixed to the ether oxygen by hydrogen bonding. The principal fat-derived hydrophobic sources are the long chain acids, alcohols, and amides.

Several papers presented as part of this Short Course have covered various aspects of the technology of nonionic surfactants, specifically the paper on ethoxylation by G.J. Stockburger, the paper on detergent additives by A. Cahn (mono- and diethanolamides), and the paper on polyglycerol esters by R. McIntyre. The simplest polyol surfactants are the monoesters of ethylene and propylene glycol. Polyethylene glycols with molecular weights up to 5-6000 have also been used in such esterification reactions.

The esters of certain sugar alcohols, such as sorbitol and manitol, represent a group of widely used nonionic surfactants. When a fatty acid is reacted with sorbitol or manitol, both internal etherification and esterification occur yielding an anhydro-hexitol ester surfactant. The formation of internal ether linkages is characteristic of sugar alcohols. Anhydro-sorbitol esters of lauric, palmitic, stearic, and oleic acid are known as "Spans." Ethoxylation of these relatively lipophilic anhydroesters at available hydroxyl groups leads to the formation of another group of commercially important surfactants, the "Tweens." These polyol surfactants are widely used as emulsifiers, wetting agents, lubricants, and detergents. They are mild and many have very low levels of toxicity and have been approved by the F.D.A. for use in pharmaceuticals, foods and cosmetics. Other areas of applications include agricultural chemical formulations, metal protection, textile applications, polymerizations, emulsions, antifoaming agents, etc. Recently, there have been reports that trace amounts (ppb range) of the potentially toxic dioxin have been detected in some ethoxylated products. Procedures to eliminate this material are being developed.

Amphoteric Surfactants

Amphoteric surfactants contain both an anionic and a cationic group in the same molecule. Compounds of this type have been known for many years and many examples have been reported in the literature, but only a few have become commercially important. In 1975, 14 million pounds of amphoteric surfactants were produced in the U.S. The relatively high cost of these materials has restricted their use to specialty applications.

One of the early examples in this category are the N-alkyl-beta alanines, prepared by the reaction of a fatty amine with an acrylic ester, followed by hydrolysis. Betaines are obtained by the reaction of fatty tertiary amines with sodium chloracetate. Amphoteric surfactants made from fatty imidazoline derivatives have found important uses in so-called mild baby shampoos.

Fatty amine oxides have the general structure $RRRN \rightarrow O$. The amines are highly polar substances with strong tendencies to hydrogen bonding. As a result, they tend to be hydroscopic and difficult to dry. Amine oxides do not show any particular oxidative activity and are quite stable when combined with other organic materials in detergent formulations. Commercial examples of fatty amine oxides include dodecyl dimethylamine oxide, N-dodecyl morpholine oxide, cocoamidopropylamine oxide, and 1-hydroxyethyl-2-octodecyl imidazoline oxide. These products have found uses in shampoos, light duty liquid detergents, and softener formulations.

The complexity of the reactions, the wide variations in the fatty acid chain, the large number of mixtures possible, the effect of processing conditions on end product composition and properties is responsible for the large number of products on the market and the myriad of trade names that we encounter. This is well illustrated by a look at McCutcheon or the CTFA Dictionary, the bible of cosmetic ingredient labeling. They list literally thousands of trademarks and hundreds of manufacturers, all offering similar chemicals that may differ in small, but significant ways in their composition, and more important to the customer, in the properties that they impart in a particular application. "Caveat emptor" is no empty warning to the users of these materials!

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