Composition and Properties of Specialty Surfactants

C. E. STEVENS, General Aniline and Film Corporation, New York, New York

IN THE SELECTION of specialty surfactants for this discussion, emphasis was placed on recent growth trends as well as on sales volume. Although most of the products described have distributed use patterns, syndets with good detersive properties were given preference. Surfactant types discussed in other papers at the short course were omitted as were the uses of specialty surfactants since these are also covered in other papers.

C. E. Stevens

The commercial acceptance of a surfactant depends upon the composite of its total properties. Markets for many chemicals with excellent surface-active properties are limited by nonsurfactant characteristics of the materials or by cost. In the manufacture of surfactants, intermediates and processes are selected to yield an optimum balance of total properties in the finished product.

The list of nonfunctional properties of surfactants includes properties dependent on the intermediates or the process of manufacture as well as on properties characteristic of the chemical composition of the surfactant. Influenced by the process and intermediates used are color, odor, inorganic-salt content, and unsolubilized-hydrophobe content. Characteristic of the chemical composition are toxicity, skin irritation, eye irritation, corrosiveness to metals, stability to hydrolysis, and compatibility in sales formulations.

The principal functional properties of surfactants are often subject to major variation within a given chemical structure. Means of achieving this variation include the following: a) in anionics, selection of the cation, *e.g.*, calcium salt *vs.* sodium salt; b) in all types, variation in the molecular weight and structure of the hydrophobe, *e.g.*, lauric acid derivatives *vs.* oleic acid derivatives; and c) in certain types, variation in the hydrophilic balance, *e.g.*, degree of sulfonation of aromatics. Since most commercial surfactants are mixtures of compounds of similar structure, it is often possible to obtain products of superior performance with respect to a preferred combination of functional properties through the proper selection of intermediates and process conditions. The principal functional properties of surfactants are foam, lather, detergency, emulsification, wetting, spreading, suspending power, dispersing action, and response to builders.

The following discussion of specific surfactant types cites functional and nonfunctional properties which are characteristic of both the chemical composition and the method of synthesis.

Sulfate Esters of Nonionics

The sulfate esters of nonionics contain two variables in the hydrophilic group, the amount of combined ethylene oxide and the capacity to form salts with a variety of bases. Products may thus be tailored to emphasize many different combinations of functional properties. However most commercial products of this type are designed for use as high-foaming detergents in light-duty formulations. This is probably because of an unusually favorable combination of functional and nonfunctional properties, *e.g.*, mildness to the skin, light color, good detergency, and high foam in dilute solutions. Sensitivity to hydrolysis under acid conditions is the principal limitation of this surfactant type. These products are usually sold as concentrated aqueous solutions or slurries which may contain as much as 5 to 20% of ethanol or isopropyl alcohol.

Sulfation increases the water solubility of nonionics to approximately the same degree as that which may be achieved with seven moles of combined ethylene oxide. Most of the nonionic surfactants used as bases for sulfation do not contain enough combined ethylene oxide to make them water-soluble. The ethylene oxide content of nonionic bases is adjusted so that the optimum hydrophobic-hydrophilic balance is obtained after sulfation. This method of solubilization is applicable especially in the case of hydrophobes to which sulfation alone does not impart sufficient water solubility for good performance, *e.g.*, tallow alcohol.

Sulfate esters of nonionics are manufactured commercially from several different hydrophobic bases and by a variety of processes. In the following paragraphs of this section four alternative methods of synthesis are described. For most products in this category the hydrophobe is either an alkylated phenol having from 8 to 12 carbon atoms in the alkyl group or an aliphatic alcohol having from 12 to 14 carbon atoms. The mole ratio of combined ethylene oxide to hydrophobe usually varies from 1 to 6, depending on the molecular weight of the hydrophobe and on the solubility required in the finished product. The cation may be ammonium, sodium, potassium, calcium, or an organic base.

In the method of synthesis shown below, sulfamic acid is reacted with a nonionic to yield directly an ammonium salt of a sulfate ester.

$$R(OCH_2CH_2)_nOH + HOSO_2NH_2 \longrightarrow R(OCH_2CH_2)_nOSO_3NH_4$$

The conversion is almost quantitative, and a slight excess of sulfamic acid suffices to hold to low limits the content of unsulfated nonionic in the finished product. The reaction is usually carried out by adding finely ground, anhydrous sulfamic acid to the anhydrous nonionic at 90–150°C. with good agitation under a blanket of inert gas. The resulting concentrated ammonium salt of the sulfate ester is frequently diluted to sales strength with water or alcohol before it is discharged from the reactor. This process is applicable to both aliphatic alcohol- and alkylphenol-derived nonionics but, because it avoids the possibility of ring sulfonation, is especially advantageous for the latter. The products obtained by the sulfamic acid process are light in color, low in odor, and low in content of inorganic salt and unsulfated nonionic.

Nonionic sulfates may be synthesized by the conventional reactions shown below, which utilize chlorosulfonic or sulfuric acid as the sulfating reagent.

$$R(OCH_2CH_2)_nOH \xrightarrow{Cl\text{-}SO_3H} R(OCH_2CH_2)_nOSO_3H \xrightarrow{\text{neutralize}} R(OCH_2CH_2)_nOSO_3M$$

$$R(OCH_2CH_2)_nOH \xrightarrow{H_2SO_4} R(OCH_2CH_2)_nOSO_3H \xrightarrow{\text{neutralize}} R(OCH_2CH_2)_nOSO_3M$$

R is an alkylphenol or aliphatic alcohol

M is NH_4^+, Na^+, K^+, or an organic amine

n is the average number of moles of combined ethylene oxide per mole of base

These processes are especially suitable for aliphatic, alcohol-derived nonionics. Ring sulfonation is a side reaction which occurs with alkylphenol-derived nonionics and frequently results in products of decreased efficiency. Sulfate esters with good color, low odor, low salt content, and good performance may be obtained with either chlorosulfonic acid or sulfuric acid. However careful control of the sulfation and subsequent neutralization is necessary to avoid darkening.

The synthesis of nonionic sulfates, with sulfur trioxide as as a sulfating reagent, is used commercially on both aliphatic alcohol-derived and alkylphenol-derived nonionics although, with the latter type, ring sulfonation as a side reaction must be minimized.

$$R(OCH_2CH_2)_nOH \xrightarrow{SO_3} R(OCH_2CH_2)_nO\text{-}SO_3H \xrightarrow{\text{neutralize}} R(OCH_2CH_2)_nOSO_3M$$

cf. previous for definitions of R, M, and n

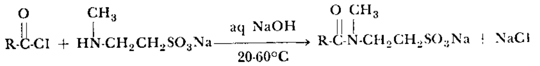
The method is advantageous because it yields directly a concentrated, salt-free acid ester, which may be converted to salts of either organic or inorganic bases. Essentially the process consists of the introduction of gaseous sulfur trioxide mixed with an inert gas (*e.g.*, air, nitrogen, methane) into the nonionic or into a solution of the nonionic in a solvent. After sulfation is completed, the acid ester is neutralized under conditions selected to minimize darkening or hydrolysis and is then diluted to sales strength.

Sodium N-Acyl-N-Methyltaurates

Sodium N-acyl-N-methyltaurates are produced by several manufacturers and include products in which the acyl group is derived from a variety of different fatty acids and mixtures of fatty acids. The water solubility, lathering, detergency, and suspending power of the sodium N-acyl-N-methyltaurates closely resemble those of the soaps of the corresponding fatty acids when these soaps are used in soft water. However the taurates are effective in hard and soft water and have stronger wetting action. They are compatible with soaps and are good lime-soap dispersants. The N-acyl-N-methyltaurates are chemically stable, and their surfactant effectiveness is unimpaired in both acidic and alkaline solutions even at elevated temperatures as well as in high concentrations of electrolytes.

Sodium N-acyl-N-methyltaurates derived from all of the common fatty acids, from lauric through stearic, are commercially available. These products are sold in the form of solutions, slurries, drum-dried flakes, and spray-dried powders. Inorganic salts are frequently used as fillers or builders in the solid forms.

Two methods are available for the manufacture of sodium N-acyl-N-methyltaurates. The method shown in the following equation is used whenever sodium chloride, which is formed in the reaction, does not adversely affect the properties of the final product.

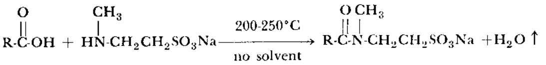


$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl + H\overset{\overset{CH_3}{|}}{N}\text{-}CH_2CH_2SO_3Na \xrightarrow[\text{20-60°C}]{\text{aq NaOH}} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{CH_3}{|}}{N}\text{-}CH_2CH_2SO_3Na + NaCl$$

pH 9 to 10

R is a C_{11} to C_{17} alkyl group

This reaction is essentially quantitative and proceeds at a rapid rate. Processes may be designed for either continuous or batch operation, and the important variables are pH, temperature, total ionic strength, and concentration of the reactants. A small excess of sodium-N-methyltaurate is frequently used to promote complete utilization of the acid chloride. The quality of the intermediate fatty acid chloride and the sodium N-methyltaurate largely determine the color, odor, and fatty acid content of the finished syndet. The intermediates are made by conventional processes. The alternative method of synthesis shown below yields a salt-free product; this is highly desirable for certain uses but has the disadvantage that an excess of fatty acid must be used.



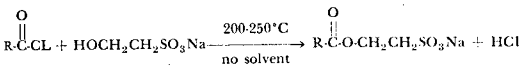
$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH + H\overset{\overset{CH_3}{|}}{N}\text{-}CH_2CH_2SO_3Na \xrightarrow[\text{no solvent}]{\text{200-250°C}} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{CH_3}{|}}{N}\text{-}CH_2CH_2SO_3Na + H_2O\uparrow$$

The product thus obtained contains a relatively high proportion, *e.g.*, 25 to 50%, of soap or fatty acid, which is difficult to remove by subsequent processing.

Sodium β-Sulfoethyl Esters of Fatty Acids

The sodium β-sulfoethyl esters of fatty acids have excellent foaming, lathering, detergent, suspending, and wetting properties. By careful selection of intermediate raw materials and control of process conditions, products can be made which are light in color, low in odor, and low in organic-salt content. However sensitivity to hydrolysis under acid or alkaline conditions, especially in aqueous solutions, limits their uses. Commercially available products include derivatives of C_{12} through C_{18} fatty acids. These are usually sold as the concentrated dry powder or as a powder containing an inorganic filler.

The synthesis of sodium β-sulfoethyl esters of fatty acids is shown schematically in the following equation.



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}CL + HOCH_2CH_2SO_3Na \xrightarrow[\text{no solvent}]{\text{200-250°C}} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2CH_2SO_3Na + HCl$$

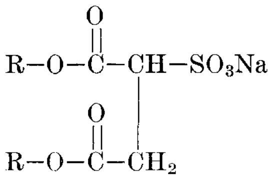
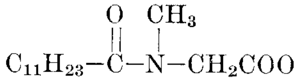
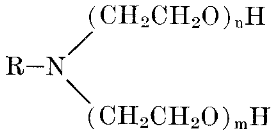
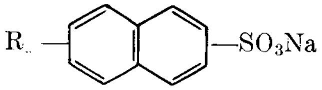
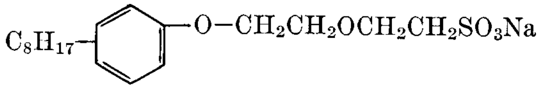
R is a C_{11} to C_{17} alkyl group

Anhydrous sodium isethionate is reacted with fatty acid chloride, in the absence of a solvent, in equipment designated to handle the transition of a viscous paste to a dry powder while maintaining good mixing and permitting the rapid evolution of dry hydrogen chloride. Since most of the hydrogen chloride formed in the reaction is volatilized, addition of dry or concentrated aqueous alkali to adjust the pH yields a solid product of low inorganic-salt content. An excess of sodium isethionate may be used to promote the complete conversion of a pure acid chloride, thus concentrations of active ingredient as high as 90% may be obtained. A grinding or milling process is generally used to obtain a sales product of uniform particle size and appearance. Inorganic salts are frequently added as fillers prior to grinding.

Amphoteric Surfactants

Amphoteric surfactants of the type shown in Fig-

TABLE I
Other Specialty Surfactants

Name and/or structure	Comments
1)  $R{-}O{-}C({=}O){-}CH(SO_3Na){-}CH_2{-}C({=}O){-}O{-}R$	A class of strong wetting agents R varies from C_4 to C_{10}
2)  $C_{11}H_{23}{-}C({=}O){-}N(CH_3){-}CH_2COONa$ Sodium N-lauroyl sarcosinate	Detergent and lathering agent for corrosion-inhibiting properties toward ferrous metals; low in toxicity and skin irritation
3) Glyceride sulfates	Detergents and lathering agents
4) Dioctadecyldimethylammonium chloride	Cationic softener and finish
5) 	Cationic surfactants with a wide variety of properties, including corrosion inhibition R varies from C_{12} to C_{18}
6) 	A class of moderately strong wetting agents R varies from C_3 to C_9 and n from 1 to 4
7) 	Stable wetting agent and detergent

ure 1, although small-volume items as compared to total surfactant market, have grown rapidly in a distributed use pattern since their relatively recent introduction. Products in this homologous series vary in functional properties from detergents with moderate foaming power to softeners and lubricants. They are usually manufactured from high-quality intermediates and are light in color, low in odor, and low in inorganic-salt content. One unusual property of this series of amphoterics is their ability to reduce eye irritation in formulations containing surfactants solubilized with sulfate or sulfonate groups. The amphoterics are compatible with anionics, cationics, nonionics. The solubility in aqueous solutions varies with pH; the products are least soluble at pH 7 ± 0.5, where inner salt formation occurs. This property is utilized in some applications. Lauric and myristic acid derivatives are usually employed in aqueous processing, whereas higher fatty acid derivatives are used as textile finishes.

Figure 1 shows schematically the synthesis and chemical structure of this series of amphoterics. Processes of manufacture and uses of the derivatives containing the imidazoline ring and a quaternary nitrogen are described in a recent series of U. S. patents issued to H. Mannheimer. Products with an open-chain structure are generally similar in properties to the imidazoline quaternaries derived from the corresponding fatty acids although surfactants of the latter type are preferred for most uses. Because of the small number of producers, detailed comments on methods of manufacture have been omitted.

Petroleum Sulfonates

Petroleum sulfonates are not properly classified as specialties but rather comprise a large-volume class of surfactants. Although originally by-products from the refining of crude petroleum, these surfactants are now manufactured as primary products conforming to rigid functional and nonfunctional specifications as required for different types of major uses. Chemically the petroleum sulfonates are complex mixtures obtained by the treatment of petroleum fractions with sulfuric acid, followed by neutralization, separation according to solubility, and purification. Petroleum sulfonates may be roughly classified into two subgroups, a) the oil-insoluble sulfonates or "green soaps" and b) the oil-soluble sulfonates or "mahogany sulfonates." The oil-soluble sulfonates are the more important products and have found extensive use in nonaqueous systems because of their favorable combination of properties. These include hydrocarbon solubility, emulsification, detergency, suspending power, and corrosion inhibition.

Other Specialty Surfactants

Any relatively brief description of specialty surfactants must limit the products discussed in some arbitrary fashion. Table I has been included to supplement the relatively detailed preceding sections by listing in tabular form other specialty surfactants with their structure and properties. Some of the products shown in this table are manufactured in greater volume and are more widely used than the materials previously described. For example, items 4) and 5) of Table I are illustrations of the large class of cationic surfactants. Most cationics are adsorbed on metals, textiles, glass, minerals, etc., and their uses are associated with this property as in corrosion inhibition and ore flotation. The properties

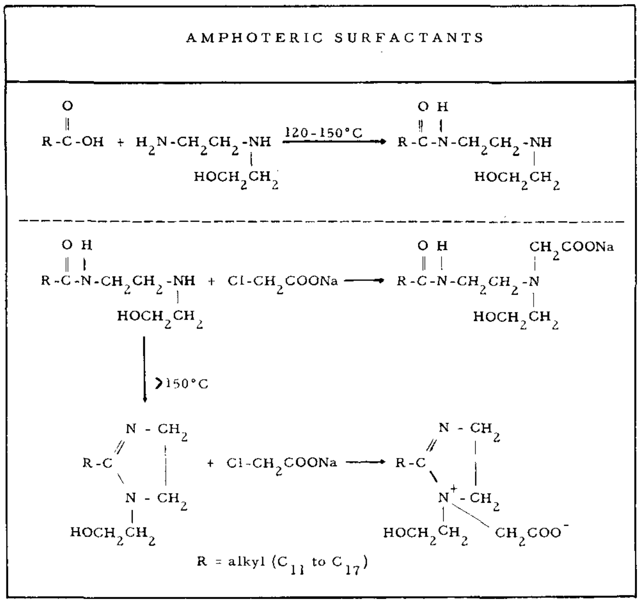


FIG. 1.

of cationics make this group of surfactants most suitable for nondetersive uses. Items 1) and 6) of Table I represent a strong, and a moderately strong wetting agent, respectively, in structures characterized by low detersive efficiency.

Summary

Surfactant chemistry is now in a market-development phase. New uses are being found and exploited for most of the numerous and diverse products that are being offered for sale. At the same time the total volume of products going into established uses is increasing. In this marketing period the volume attained by each competitive type depends on its composite of functional and nonfunctional properties as well as on its cost. In many cases nonfunctional rather than functional properties determine which process of manufacture or which surfactant type will attain the predominant position in a given market.

Acknowledgments and Comments

The author is indebted to many associates in the General Aniline and Film Corporation for assistance in the preparation of this paper, especially to R. L. Mayhew and Mrs. E. A. Parolla. The information is presented as a review of current commercial practices for the convenience of new workers in the field of surfactant chemistry. References have been omitted because Schwartz, A. M., Perry, J. W., and Berch, J., in "Surface-Active Agents and Detergents," vol. II, have recently and comprehensively reviewed the technical literature in this field.

Specialty Surfactant Applications

GEORGE E. BARKER, Quaker Chemical Products Corporation, Conshohocken, Pennsylvania

ALTHOUGH the most heavily consumed syndets, including alkylaryl sulfonates, alcohol sulfates and ethylene oxide derivatives of tall oil, alkylphenols, and alcohols are employed broadly, other particular surfactant structures are more efficient for many specialized applications. This discussion will attempt to point out some of the most effective structures for special applications even though the more common soaps and syndets are sometimes employed for these very specialized uses. For example, occasionally sodium dodecyl benzene sulfonate is used as a true wetting agent in textile applications although it is not as efficient as the alkyl sulfosuccinates or the secondary alcohol sulfates. As has already been described, synthetic organic chemistry has made available syndets with such wide variations in structure that almost any combination of surface-active properties is available.

G. E. Barker

This discussion will be divided into the principal applications, using primarily specialty surfactants. All applications to the textile field will be omitted since they are being covered elsewhere in this course. Phases of the following applications are now being considered: dishwashing detergents, synthetic detergent bars, maintenance cleaners, dairy cleaners, metal cleaners, drugs and cosmetics, foods, dry cleaning, agricultural chemicals, leather processing, and petroleum applications. The specialty syndets to be discussed will be chiefly restricted to the following classes: syndets having a modified or "blocked" carboxyl group: a) polyhydric alcohol esters, b) sulfated esters, and c) sulfonated amides; sulfated ethers; alkylnaphthalene sulfonates; petroleum sulfonates; dialkyl sulfosuccinates; sulfated branched chain alcohols; polyoxyalkylene ethers; quaternary ammonium compounds; amine salts; polyoxyethylene amines; polyoxyalkylene esters; and alkylol amides.

Since there are special conditions of application for each industry in which these specialty syndets are employed, this discussion will be divided by application. The specialty syndets particularly suitable for each application will be emphasized. Table I summarizes the relationship between individual syndet and its application.

Agricultural Chemicals

In the field of agriculture syndets find their principal uses as emulsifiers for solvents carrying the toxicants, fungicides, or herbicides in solution. Important criteria are ease of emulsification, wetting of the foliage, low phytotoxicity, and stability of the emulsion. Since this is primarily an emulsification prob-