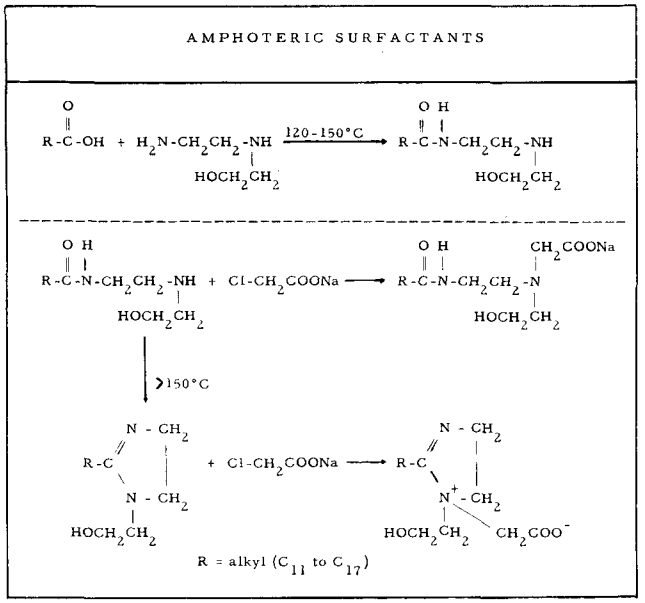

FIG. 1.

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

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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.

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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-

lem, it is one of selecting a surfactant or mixture of surfactants of the proper chemical structure and proper balance between the hydrophilic and lipophilic character of the emulsifier. Although the standard volume-produced syndets are sometimes employed, the principal surfactants used are special nonionics of the polyether alcohol or polyhydric alcohol ester type with or without the addition of alkylaryl sulfonates, usually as amine salts. Examples of these are some of the Tritons, Emulphors, and the Atloxes.

Dairy Cleaners

The cleaners most used in dairies are the highly alkaline mixes with a small quantity of conventional wetting agent or detergent and often sequestering agents. Dairy cleaners are considered in this discussion chiefly because of the use of surface-active germicides and sanitizers. Quaternary ammonium compounds, such as lauryl benzyl dimethyl ammonium chloride (Roccal or Hyamine), have been employed in germicidal rinses and sanitizers for many years. The important precaution is to prevent inactivation by soaps and other anionic surfactants. Although sometimes detergent-sanitizers for simultaneous cleaning and sanitization are employed, they are neither as economical nor as reliable as separate cleaning, followed by a germicidal rinse. A relatively new surface-active germicidal agent has been made available in the form of iodine complexed with a nonionic surfactant. These products are not effective in alkaline solution. However they are effective sanitizers in acid media and thus are useful in sanitizing dairy equipment. One of these products is Biopal VRO-20.

Dishwashing Detergents

With the introduction of Glim more than 10 years ago the liquid dishwashing detergents were established. The first formulation of this product was based on a nonionic detergent which lacked foaming power and foam stability, a real deficiency in the eyes of the housewife. In the years since that first pioneering work light-duty liquid detergents that produce copious foam and rinse freely have been developed. Most of these newer products contain sulfated polyoxyethylene ethers, such as the Alipals. To stabilize the foam, generally an alkylolamide, such as Dianol G or Ninol, is added. Recently polyoxyethylene tridecyl alcohols have been reported, used with the sulfated polyoxyethylene alkyl phenols as liquid dishwashing detergents to give copious, stable foam. Although these types of formulations are the most common, the more conventional alkylbenzene sulfonates and alcohol sulfates, generally as amine or ammonium salts, are sometimes employed in various formulations. Hand dishwashing in restaurants, taverns, and soda fountains is generally followed by a sanitizing rinse, often consisting of a quaternary ammonium germicide of the type described under dairy cleaners. In this operation a rinse in clear water before going into the sanitizing bath is recommended. Sometimes detergent-sanitizers are employed in which combinations of built nonionic detergents and quaternary ammonium germicides are commonly used.

Detergents for machine dishwashing are composed mostly or sometimes entirely of alkalies. In some of the better products syndets are incorporated to the extent of 2 to 15%. The syndets employed are chiefly low foaming nonionics, such as polyoxyethylene tall oil (Sterox CD) and the polyoxyalkylene glycols (Pluronics). A more recent development is the introduction of rinsing aids preferably through a rinse injector system to promote rapid draining of water and consequently drying free of spots. This has been particularly effective in reducing the spotting of plastic dinnerware. For this purpose only the very lowest foaming nonionics are suitable. Examples are Pluronic L-62 and Triton Cf-10.

Drugs and Cosmetics

One of the earliest applications for specialty surfactants was in the preparation of cosmetics. The most widely distributed shampoos are based on ammonium or amine salts of the alcohol sulfates, sometimes with the addition of foam stabilizers, such as the alkylolamides. In more recent years shampoos having germicidal properties, absence of eye irritation, and other special properties have been developed. Some of the quaternary ammonium germicides have been combined with nonionic detergents to produce a germicidal shampoo. One word of caution: the quaternary ammonium salts tend to be severe eye irritants, and some of the conventional nonionics also cause eye irritation and sometimes damage at higher concentrations. Consequently every shampoo should be submitted to tests for eye damage by the procedure of Draize, Woodward, and Calvery. Generally the water-soluble esters of polyhydric alcohols are the least irritating to the eyes.

The most extensive use of specialty syndets in the cosmetic field is for the preparation of emulsions. It is true that soaps and the more standard bulk syndets have been used widely and still are used for preparing emulsions, but the specialty products are employed to obtain better shelf-life, improved control of viscosity, ease of manufacture, and special properties. Traditional cold creams, for example, are generally of the O/W type of emulsion and contain mineral oil, natural or synthetic waxes, and water emulsified with a moderately hydrophilic syndet, such as an alkylolamide, polyoxyethylene ether or ester, alone or combined with soap or conventional syndet. These basic formulas are modified with perfumes, emollients, ultraviolet absorbents, antiperspirants, etc., for special purposes. With the development of the specialty surfactants capable of preparing W/O emulsions, cold creams of the W/O type became possible and quite popular, principally because of their decreased tendency to dry out. The basic formula contains mineral oil, a wax, water, and a W/O emulsifier, such as glycerol mono-oleate, sorbitan mono-oleate, or a glycol fatty acid ester. These basic formulas are modified to produce a hair dressing, cream rouge, lip pomades, etc.

In the pharmaceutical field specialty syndets are used to prepare ointment bases, similar to the two types of cream formulas, to carry medicaments such as the sulfanilamides, antibiotics, analgesics, and other drugs. Another application of specialty syndets is for emulsifying oil-soluble vitamins in water so that both oil- and water-soluble vitamins can be dispensed in the same medium. Hydrophilic or water-soluble surfactants are used to solubilize essential oils, such as oil of peppermint or oil of cloves in water. The most widely used surfactants for these purposes are polyoxyethylene derivatives of fatty acids and alcohols. It perhaps should not be forgotten that the

quaternary ammonium germicides, such as Zephiran and Ceepryn, are used in the drug industry as germicides.

In more recent years some specialty syndets have found direct application as active medicaments. One sample is polyoxyethylene sorbitan mono-oleate (Polysorbate 80, U.S.P.), which is prescribed by physicians to increase the absorption of fats. Deficiencies in fat absorption are inherent in several conditions affecting the function of the small intestine, such as a major loss of absorptive surface, secondary to an inflammatory process or to short-circuiting operations. More recently sodium di-2-ethylhexylsulfosuccinate has found use as a laxative. It apparently functions by its surface activity, producing a softer faeces.

Dry Cleaning

Specialty syndets find a substantial market in dry cleaning. In dry cleaning the solvent, either petroleum or chlorinated, removes the solvent-soluble soils. Solubilized or emulsified water removes the water-soluble soils. The detergent and mechanical action remove and maintain in suspension the insoluble soils. Most dry cleaning now is accomplished in the "charged system," where the solvent is charged with 0.5 to 4.0% detergent. The charged solvent is used continuously with frequent additions of detergent to maintain the concentration. This system is characterized by high water-soluble, soil removal and economy of operation. Petroleum sulfonates of medium molecular weight were the first detergents to replace paste soaps. Some synthetic alkylaryl sulfonate detergents, especially in the form of amine salts, have been used very successfully. Other anionics, which have been used in dry cleaning, include sulfated amides and esters as well as sulfonated amides. In recent years oil-soluble, nonionic detergents of the polyhydric alcohol ester type, the alkylaryl polyglycol ether type, and to some extent the alkylolamide type have been used in increasing quantities. Blends of nonionic and anionic detergents are also used.

Foods

The incorporation of surfactants in foods has been a somewhat controversial subject. Although some naturally occurring surfactants (lecithin) are present in food, the really effective surfactants in food are the synthetic ones. The most common products used in baked goods (bread, cake, etc.) are the monoglycerides of fatty acids. They improve the texture, retard staling, and enhance the effectiveness of the shortening. The same products are used in ice cream to increase the air content, improve the smoothness, and enhance the palatability. Other products, until banned by the Food and Drug Administration, mostly polyoxyethylene derivatives of fatty acids and esters of polyhydric alcohols, have been used extensively with great effectiveness. These latter products are used in chocolate coatings to reduce the bloom. They have also been used in preparing various sauces and dressings where they serve chiefly as emulsifiers.

Leather Processing

In leather and fur processing the skins of animals are converted into furs or leather by a series of steps, consisting essentially of salting, soaking, scouring, fleshing, tanning, bleaching, dyeing, fat-liquoring or oiling, and finishing. Syndets are used in several of these processes. They are used in degreasing in aqueous solution or sometimes in solvents. In the latter case sulfated esters are often used. Sometimes salt is added to effect reversal of the emulsions to the O/W type, which can be readily washed out. Cationic syndets, such as cetypyridinium bromide, have been used in aqueous solution for effective degreasing.

Another step which employs surfactants is the actual tanning, where alkyl naphthalenes condensed with formaldehyde and sulfonated are the most widely used "syntans." Alkane sulfonyl chlorides have also been used for preparing white and chamois leathers. In dyeing furs and leather, the substantive dyestuff is applied in an aqueous solution containing such specialty syndets as oleic methyl tauride or the sulfates of glycerol monoesters. It is necessary to add oils or fats to fur or wool skins to make them soft and to give the fibers a high gloss. This is called fat-liquoring and is accomplished by a process of treating the tanned pelts with O/W emulsions. The emulsifiers used to prepare these emulsions may advantageously include blends of cationic complex amide condensation products, with nonionic detergents or petroleum sulfonates. Where stability to low pH is required, polyoxyalkylene sorbitan esters or 1-hydroxyethyl-2-heptadecenyl-imidazoline may be used.

Maintenance Cleaners

Although by far the majority of cleaners used for general building maintenance are based on the commodity type of detergents, there are some specialty syndets employed for particular purposes. In floor cleaners particular attention must be paid to possible damage to some of the materials used in floor construction. Asphalt tile and linoleum are especially subject to damage. In some of these cleaners alkylol amides, sulfated polyglycol ethers, and fatty amide alkane sulfonates are used. For grease removal on concrete floors emulsifiable solvent cleaners are sometimes employed. One of the best products of this type is a mixed orthodichlorobenzene and high flash naphtha or kerosene solvent containing an emulsifier such as a polyoxyethylene polyhydric alcohol fatty acid ester (Tween 85, for example). In maintaining floors it is customary to apply waxes. Specialty syndets are often used in preparing the waxes. Although amine soaps are widely used as emulsifiers, many times mixtures of polyoxyethylene polyhydric alcohol esters are employed either alone or added to the soap.

Metal Cleaning

Most metal products require cleaning at many stages during processing and fabrication. The type of cleaning and cleaning agent depends on the soil, the cleaning equipment available, and the degree of cleanliness necessary. There are two fundamentally different cleaning operations; one uses organic solvents and the other uses water. They both may or may not use syndets although it is widely believed that either solvent may generally be improved by the addition of suitable surfactants. Organic solvents alone are generally used in soak tanks or vapor degreasing equipment. The latter process consists of allowing vapor from boiling solvent to condense on the soiled metal and flow back into the vaporizer. Generally chlorinated solvents are used to eliminate fire and explosion hazards. Surfactants are often

added to organic solvents, especially for soak tank or spray application, to make them emulsifiable. This type of cleaner operates by dissolving the oil, grease, and wax from the metal surface and rinsing with hot water to form an emulsion which carries away the insoluble soil. It also removes any water-soluble soils, such as inorganic salts. The other type of cleaner using solvents is the emulsion cleaner. In this case concentrates of emulsifier in the solvent are diluted with 10 to 100 parts of water. At times alkalies are added in low concentrations to these baths to improve cleaning.

The chief portion of the emulsion cleaner is the solvent, which may be a hydrocarbon, such as kerosene and high flash naphtha, or a chlorinated solvent, such as trichloroethylene or perchloroethylene. Emulsion cleaning is intended to remove the bulk soil from the metal. Generally the emulsion cleaner deposits an oil film on the metal, and, if properly formulated, this film will inhibit rusting. The possibility of laying down a rust preventive film is one of the principal incentives for the use of emulsion cleaners. In those instances where an oil-free surface is required, the emulsion is followed by an alkaline cleaning just prior to final finishing, such as electroplating. Quite a wide variety of emulsifiers are used for emulsion cleaners. The mahogany soaps or petroleum sulfonates are the most widely used. They are inexpensive and have good rust-inhibiting qualities. Blends of nonionic emulsifiers of ethylene oxide condensate type are becoming more popular because of their low-foaming character. Often "coupling agents," such as glycol ethers, are useful in preparing a clear, stable concentrate.

Occasionally emulsion cleaning is combined with phosphating which is used to improve adhesion of paints, lacquers, or enamels to metal surfaces. Phosphating also improves the resistance of the steel to corrosion. Generally nonionic emulsifiers of the ethylene oxide condensate type are used for emulsion cleaners containing acid phosphates.

Sometimes unstable emulsions of solvents in water are used for metal cleaning and are designated diphase cleaners. They are prepared by using a very small amount of emulsifier and remain emulsified only when well agitated. Properly formulated diphase cleaners are exceedingly effective soil removers and sometimes approach straight solvent cleaners in efficiency.

Synthetic Detergents in Bar Form

Only recently have synthetic detergents made any progress in entering the household, toilet, or laundry bar market. The principal advantages of synthetic bars over soap bars are found in their ability to lather profusely in hard water and in the fact that they do not form insoluble deposits of soil on the basin or bath tub. The synthetic detergent bars are for convenience grouped into two classes, the "all synthetic" and the soap-synthetic mixtures.

Some all-synthetic detergent bars have been placed on the market, principally as drug items, for those people who are allergic to soap. Some of these bars contain such detergents as glycerol fatty acid ester sulfates, fatty acid amide alkane sulfonates, dialkylsulfosuccinates, and polyoxyethylene alkyl ethers. It is usually necessary to add some binder to give the bar a satisfactory consistency, strength, and rate of dissolution. Common binders and modifiers for synthetic detergent bars include sodium carboxymethyl cellulose, cellulose ethers, vegetable gums, corn starch, and lecithin. One approach which has been suggested is the preparation of solid complexes of urea with polyoxyethylene alcohols in bar form with modifiers to reduce the rate of solubility.

The armed services have favored the soap-synthetic bars. In fact, the first synthetics in bar form were combinations of soap and alkylaryl sulfonates, the development of which was sponsored by the Armed Services during World War II. Although serviceable, these bars had many disadvantages. More recent improved versions of these sea water detergent bars, still containing about 50% soap, contain isopropylnaphthalene sulfonate and diamyl sulfosuccinate along with dodecylbenzene sulfonate. Most of the synthetic bars on the market are compositions which are not revealed although one bar, Vel Beauty Bar, discloses on the label that the active ingredient is sulfated coconut fatty acid esters of glycerol.

Petroleum Applications—Production

Drilling Fluids. Specialty surfactants are applied in the petroleum industry from the drilling of the well to the preparation of slushing oils. This industry affords the most diverse applications of specialty surfactants.

Oil wells are drilled with rotary bits. A fluid is circulated down the drill pipe, through nozzles in the bit and upward through the annular space between the pipe and the walls of the hole. The chief function of this drilling fluid is to carry the chips or cuttings to the surface. Other functions include cooling the bit, supporting the walls of the hole, and holding back the liquids and gases in the formations which are being penetrated. There are three principal types of drilling fluids: the water-base, the oil-base, and the emulsion fluids.

The water-base, which is the simplest and oldest, is essentially a suspension of bentonite in water with additives to control viscosity, water loss, gel strength, and thixotropy. Specialty surfactants are quite effective in controlling some of these latter properties. The lignin sulfonates are used for control of viscosity and stabilizing the muds. Sulfonated phenol-formaldehyde condensates serve the same purposes. Mahogany soaps, alkylphenol, polyetheylene glycols, polyoxyethylene esters of sorbitan, and polyoxyethylene esters of tall oil have been shown to have favorable effects on water-based bentonite drilling muds.

The emulsion type of drilling fluid is made by adding 5 to 30% oil to the water-base mud with emulsifier. The latter may be one of the surfactants listed above or any of several other water-soluble sulfated or sulfonated surfactants.

The oil-base drilling fluid consists of diesel fuel oil or crude oil thickened with gelling agents. The gelling agents are frequently bentonites, which are made oleophilic by treatment with a cationic surfactant. Sometimes the gels have been made by adding water with a W/O emulsifier. The latter may be a polyhydric alcohol partial ester or a mixture of such an ester with polyoxyethylene derivatives.

Acidizing Oil Wells. Often the flow of oil can be increased by treating a formation with acid to dissolve lime deposits or shrink clays. Although a variety of acids have been used for treating oil wells,

hydrochloric acid is probably the most widely employed. Wetting agents speed the action of the acid. Cationics of both the amine and quaternary ammonium type, anionics of almost all types, and nonionics of the polyoxyethylene ether type are used.

Hydraulic Fracturing. Another method of rejuvenating the productivity of some oil wells involves the pumping of a viscous fluid into the well under pressure sufficient to crack the formation and thus create fissures through which the petroleum can flow to the well bottom. After fracturing, it is considered necessary to reduce the viscosity or break the gel, if it is the latter type, to prevent clogging of the passage ways. Gelled petroleum oils, sometimes augmented by suspended sands or other finely divided solid material, are most frequently used. The oil is sometimes gelled with soaps to produce a gel similar to Napalm, which was used in fire bombs. This gel can be broken by introducing petroleum sulfonates.

A rather unique, combined acidizing and fracturing technique was developed where hydrochloric acid was gelled by mixing with crude petroleum or diesel fuel in the presence of a water-in-oil emulsifier. The viscosity of the emulsion or gel is partly controlled by the ratio of aqueous acid to oil. The really clever application of this technique is the use of a monofatty acid ester of a polyhydric alcohol as the emulsifier since in a few hours the acid decomposes the emulsifier and the gel liquefies and flows out of the well with the crude oil.

Secondary Oil Recovery. Secondary oil recovery is the process of increasing crude oil production through the application of energy from external sources. When the external source is water under pressure, the process is called water-flooding. Many oil fields, whose natural recovery of oil has ceased, have been water-flooded to recover almost as much oil as originally produced. Even under ideal water-flooding conditions about one-third of the original crude is left in the reservoir.

The failure of water-flooding to displace essentially completely the oil present is now believed to be caused by capillary forces operating within the formation. The capillary forces involved are generally described as the interfacial tensions present at the phase boundaries. In short, it is necessary for the water preferentially to wet the mineral surface and thus displace the oil. The most popular surfactants in these experimental programs are the polyoxyethylene nonionics of the alkylphenol types, fatty ester, and fatty amide types. Recently it has been shown that the whole of the flooding water need not be treated with the surfactant but that a slug or plug of treated water be pushed ahead of the bulk of the water used for flooding. This makes the process look much more feasible from the economic point of view. It has been estimated that if surfactant flooding were employed in areas where water flooding is economically feasible, it would create a market for 20 billion pounds of surfactants.

There is a current market for quaternary ammonium germicides in water-flooding operations to prevent the growth of bacteria and algae which may interfere with the injection of water. In addition to the quaternary ammonium compounds, rosin amine and its polyoxyethylene derivatives have been used in flood waters for a similar effect. These same compounds combine corrosion-inhibiting properties, especially in acid sysytems, with their bactericidal and fungicidal properties.

Demulsification of Crudes. Crude petroleum is often emulsified with water or brine. It is necessary to separate the oil from the bulk of the water or brine; this is accomplished most generally by the addition of emulsion breakers. There is voluminous patent literature on this subject, but it is largely an empirical art. The crude emulsions appear to be stabilized by a variety of agents, including inorganic solid matter, resins, asphaltenes, carboxylic acids and their salts, and metal complexes of porphyrins and oxidized porphyrins. The latter materials appear to be quite widely distributed and involve the following metals: zinc, copper, nickel, calcium, magnesium, iron, and vanadium.

A very wide variety of materials have been employed for emulsion breaking. In fact, emulsion breakers have been developed for single oil fields and even for individual wells. Among the most widely used emulsion breakers are petroleum sulfonates, polyalkylbenzene and polyalkylnaphthalene sulfonates, sulfonated terpenes, polyoxyethylene ethers and esters, amines, carboxylic acid soaps, and polymeric ester types of nonionics.

Petroleum Applications—Products

In addition to use in petroleum production, specialty surfactants are incorporated in many petroleum products, including corrosion preventives, fuels, and lubricants.

Corrosion Preventives. The most common rust-preventives are petroleum oils containing an effective quantity of a rust inhibitor. The rust inhibitors are generally oil-soluble surfactants, commonly belonging to one of three classes: the mahogany sulfonates, carboxylic acids and their salts, and esters of carboxylic

TABLE I
Applications of Specialty Surfactants

	Polyhydric alcohol esters	Amopholytic syndets	Sulfated esters	Sulfonated amides	Sulfated ethers	Alkylnaphthalene sulfonates	Petroleum sulfonates	Dialkyl sulfosuccinates	Sulfated branched chain alcohols	Polyoxyalkylene ethers	Quaternary ammonium compounds	Polyoxyethylene esters	Alkylolamides
Agricultural chemicals	x						x			x		x	x
Dairy cleaners		x								x	x		
Detergent bars			x	x				x		x		x	
Dishwashing detergents													
Hand			x	x	x			x	x		x		x
Machine										x		x	
Drugs and cosmetics													
Creams	x											x	
Germicides		x						x		x	x		
Ointments	x	x										x	
Perfumes										x		x	
Shampoos			x	x					x		x		x
Foods	x											x	
Leather processing													
Degreasing			x	x				x	x	x			x
Fat liquoring							x				x		
Maintenance products													
Floor cleaners				x	x							x	x
Waxes	x											x	x
Metal cleaning	x									x		x	
Petroleum—Production													
Acidizing additives							x			x	x		
Demulsifiers	x					x	x			x		x	
Drilling fluids	x						x					x	
Hydraulic fracturing fl	x						x					x	
Secondary oil recovery additives										x		x	x
Petroleum—Products													
Lubricant additives						x	x	x		x		x	
Metal working lubricants	x						x						
Corrosion preventives	x					x	x			x	x		

or phosphoric acids. The mahogany sulfonates are the most widely used, and the higher molecular weight ranges are the most effective. The sulfonates are used as alkali, alkaline earth, or amine salts. Some synthetic alkylaryl sulfonates have been found to be very effective rust inhibitors. Especially effective synthetics are the alkaline earth salts of dinonylnaphthalene sulfonic acid. Sometimes polyoxyethylene alkylphenols of proper lipophylic character are added to the extent of about 10% of sulfonates to improve their effectiveness, presumably through more uniform spreading of the rust preventive oil.

A wide variety of esters, especially partial fatty acid esters of polyhydric alcohols, show very strong rust-inhibiting qualities when applied in a mineral oil. Among these effective surfactants are sorbitan mono-oleate, glycerol mono-oleate, and pentaerythritol mono-oleate. The higher fatty acids and their soaps, as well as naphthenic acids and their soaps, are effective rust inhibitors. Polymerized unsaturated fatty acids are effective rust inhibitors and are widely used in light petroleum fractions to prevent the rusting of pipelines, tankers, and other transportation and storage vessels.

The alkenyl succinic acids, their monoesters, amine salts and substituted amide derivatives are effective rust inhibitors.

In connection with rust inhibition it is often desirable to displace water or aqueous solutions from the surface of a metal with a protective oil. This is particularly desirable when it is necessary to remove finger prints. The higher amine salts of alkyl-naphthalene sulfonic acids have proved quite useful. Other substances which have been used for this purpose include lanolin, naphthenic acids, glycol esters, and alcohols, usually in carefully prescribed combinations. Aside from the removal of finger prints, products of this type are used to remove water from metal parts as these are removed from aqueous cleaning baths.

Phosphate and thiophosphate esters and their metallic salts are very effective corrosion inhibitors in lubricants, especially for protecting the nonferrous bearing metals. These products are often used as their zinc or calcium salts.

Lubricants. One of the large uses for oil-soluble surfactants is the field of lubricants, where they are used as motor oil detergents or dispersants, in the preparation of greases, and in the preparation of metal-working lubricants.

The word "detergent" when applied to automotive and diesel engine oils is somewhat of a misnomer to describe the usual function of these oils. The detergent oils instead of cleaning the engine usually maintain a clean engine by preventing the deposition of resinous, gummy, or carbonaceous substances on the metal surfaces. The so-called detergents are generally dispersants which maintain these insoluble decomposition products of lubricants in suspension. The most extensively used lubricating oil detergents are the hydrocarbon sulfonates, either mahogany soaps or synthetic oil-soluble alkylaryl sulfonates. The calcium and barium salts are preferred, and at least some refiners prefer the basic salts prepared by using more than the stoichiometric ratio of metal carbonate or hydroxide to sulfonic acid. In recent years ashless motor oil detergents have been introduced. Some of these are based on tertiary amine alcohol esters of acrylic or methacrylic acids copolymerized with longer chain alkylacrylates or methacrylates.

Some interesting developments in the field of lubricating greases have taken place in recent years. The traditional grease is a lubricating fluid gelled with a soap. More recent developments have shown that greases can be produced by nonsurface-active gelation agents and by surfactants other than soap. For example, heavy metal salts including magnesium and aluminum salts of the alkenylsuccinic acids have been used to form greases. Some of the nonsurface-active gelling agents are rendered oleophilic by treatment with cationic surfactants, such as polyoxyethylene fatty amines, imidazolines, and quaternary ammonium salts. The silicas, clays, and bentonites have been so treated to produce satisfactory greases. The bentonites have been particularly successfully used and are known as Bentones.

Surfactants play an important role in the cutting, drawing, and rolling of metals. They may serve two purposes, as true lubricants and as emulsifiers for dispersing the lubricant in water. Although sulfurized and chlorinated oils are incorporated in many metal-working lubricants to impart extreme pressure properties, many times surfactants, such as partial esters of polyhydric alcohols, are added to impart some boundary-lubricating properties. The emulsions are used where lubricating requirements are not too severe and cooling is an important factor. The most widely used emulsifying agents in these products are the mahogany sulfonates. The petroleum sulfonates are often combined with soaps or other surfactants, such as the polyoxyethylene ethers or esters. Polyalkylene glycols have reportedly been used as cutting fluids.