We had in our Association office recently a small group of Japanese soap-makers who had formed what was called the All-Japan Soap Association. This organization was at least partially developed and sponsored by the National Renderers Association and the Department of Agriculture of the United States. It is another one of those fine examples of industry-government cooperation of benefit to the people of this country and to others. It is a highly intelligent activity to solve a very serious problem.

The change from soaps to synthetics has also had repercussions in the production of glycerine. The production of glycerine in 1940 totalled 158,000,000 lbs., of which 148,000,000 were produced by the soap industry and 10,000,000 by other sources, none of which included any synthetic glycerine. This production of natural glycerine from soap and other processes has fallen from 158,000,000 lbs. to approximately 140,000,000 lbs. in 1957. Because glycerine is a useful and valuable product, others saw in this drying up of the source of natural glycerine, industrial opportunity, and today at least two companies are producing glycerine from propylene to the extent in 1957 of 100,000,000 lbs. All sources in 1957 gave a total production of 240,000,000, an increase of about 50% from 1940.

A further trend has taken place which, while not a part of the soap industry, has a vital effect on soap-industry marketing. The distribution of soaps has changed along with all other grocery items, and today a very large and vital part of this distribution is through chain stores and supermarkets where the purchaser takes the package off the shelf and is not served by a grocery clerk. This has emphasized the importance of brand names, of advertising, of shelf display, and of package design.

The soap industry has been a leader of trends in advertising and merchandising. It has used coupons on the wrapper or package, it has had premium packs, house-to-house sampling and couponing, 1¢ sales, contests, comic strips, radio, television, and about every kind of innovation. The most recent was a New York subway ride for soap coupons.

I can recall early days where a premium or an imitation pearl necklace or other gadget for the wife of the independent grocery store owner might be the inducement to make a sale. Not so any longer. I also recall finding a method to sell an excessive amount of soap in stores along a highway from Kansas City to Bonner Springs, Kans. On my next trip I found what the chain store and supermarket know today, the whole problem of successful selling is not putting the product into the store but instead moving it off the shelf into the hands of the consumer.

We can look backward and see so clearly the trends. Unfortunately we cannot see exactly the trends which will come in the future. I cannot help but think about the sage advice given me by an older man, no longer living, who in relation to personnel changes in a company said, "it has been my observation that a young man's opportunity comes in a period of change."

A Review of Ethylene Oxide Condensation with Relation to Surface-Active Agents

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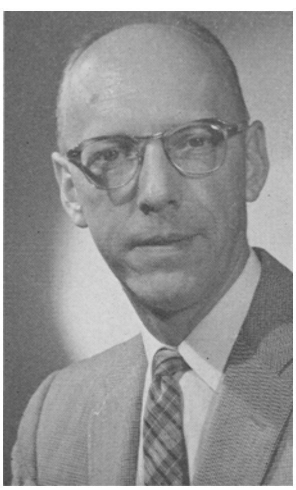
IN THE MANUFACTURE of surface-active agents, ethylene oxide condensation is one of the principal processes employed to introduce hydrophilic functional groups into the molecular structures of organic compounds. The ultimate objective of the process is the production of surface-active agents having the desired hydrophile-lipophile balance (H.L.B.) for such commercial applications as detergency, emulsification, wetting, textile processing, etc. As a means of increasing the hydrophilic propties of organic compounds, ethylene oxide condensation ranks in importance with such processes as saponification, sulfonation, sulfation, quaternization, etc.


R. D. Fine

Surface-active agents produced by these other processes dissociate to some extent in aqueous solutions, forming ions which characterize the compounds as either anionic or cationic, depending upon the electrical charge exhibited by the lipophilic component. These ions are free to react with other ions which may be present when the products are used. Such reactions can result in the inactivation of the surface-active agent and other undesirable effects. Except for certain organic amine derivatives, such ionic dissociation does not occur with ethylene oxide condensation compounds, and they are considered nonionic. In aqueous media these compounds form colloidally dispersed micelles. Although visually they may appear to be completely soluble in water, their colloidal character is demonstrated by the presence of the Tyndall effect when a beam of light is passed through an aqueous solution. Some migration of micelles of nonionic compounds may occur in aqueous media in an electrostatic field, but this is believed to result from the presence of charges on the micelles themselves with respect to the solvent rather than to the existence of ions (1). The nonionic character of these compounds greatly increases their range of compatibility with other materials that may be encountered in use. Although high concentrations of sodium ions may salt out such products from solution, most of them exhibit a high tolerance for hard water salts, and some types are stable in the presence of relatively strong acids and bases.

Another characteristic of ethylene oxide condensation compounds that differentiates them from ionic compounds is their semipolymeric structure which results from the cumulative condensation of successive molecules of ethylene oxide to form polyoxyethylene chains. The oxyethylene units achieve their hydrophilic properties through hydration of the ether-linked oxygen which they contain. The degree of hydration of these ether-linked oxygens varies inversely with the temperature when the compounds are dissolved in water. By increasing the temperature of an aqueous system containing a polyoxyethylene compound, a fairly sharp cloud-point is usually observed and is frequently used as a test in controlling the degree and distribution of ethylene oxide condensation in manufacturing such compounds and in their analytical identification.

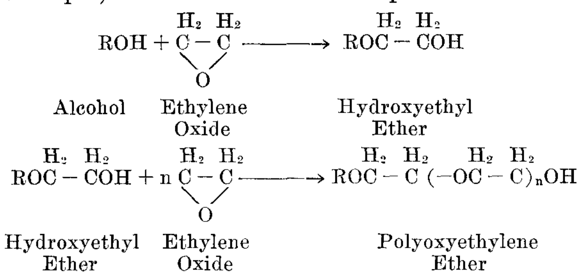
A single oxyethylene unit is considerably less hydrophilic than an ionic hydrophilic group, therefore a relatively large polymeric chain of oxyethylene units on a weight percentage basis must be condensed with a lipophilic unit in order to produce a compound with distinctly hydrophilic characteristics. Because of the relatively low cost of ethylene oxide (about $.155 per pound) and the absence of by-products in the reaction, ethylene oxide condensation is essentially an economical means of introducing hydrophilic groups in making surface-active agents.

Chemistry

In ethylene oxide condensation, the epoxide ring of ethylene oxide opens and combines with an active hydrogen atom contained in a functional group present in the compound with which it is being condensed to form a hydroxyethyl derivative. The active hydrogen of the hydroxyethyl derivative is then available for reaction with an additional epoxide group and, by repetition of this process, a polyoxyethylene compound can be formed. Alcohols, phenols, carboxylic acids, amines, amides, and mercaptans are the compounds most commonly condensed with ethylene oxide to produce surface-active agents. Using an alcohol as an example, the reaction can be represented as:

I.

II.



In the course of this polycondensation reaction a heterogeneous distribution of oxyethylene chain lengths is obtained. Under neutral conditions at high temperatures or in the presence of an acid catalyst, such as boron trifluoride, at lower temperatures, the hydroxyl groups of an alcohol and its hydroxyethyl ethers are about equally reactive to ethylene oxide (2). In the presence of a basic catalyst, such as sodium hydroxide, considerable variations in reactivity with ethylene oxide are exhibited by different alcohols and hydroxyethyl ethers. In alkali-catalyzed reactions these differences in reactivity appear to be caused by the influence of the anions dissociated by the various hydroxy compounds. Thus in the initial step of the reaction the rate is determined by the concentration of the ion RO^- and in the second step by the ion $\overset{H_2}{ROC} - \overset{H_2}{CO^-}$.

Each succeeding step involves the previously formed alkoxide ion.

Since the surface-active agents produced by ethylene oxide condensation are of heterogeneous composition they are identified by the total mole ratio of ethylene oxide to lipophile. Thus when a product is characterized as containing a specified number of oxyethylene groups or moles of ethylene oxide per lipophilic group, it means that ethylene oxide has been added to the lipophile until an amount has been absorbed which is equivalent to the specified mole ratio. The average molecular weight of such a compound corresponds closely to the theoretical value for the specified mole ratio, but the actual distribution of oxyethylene groups among the individual molecules closely follows Poisson's distribution formula (3). It is probable that the functional properties generally identified with various commercial polyoxyethylene products are caused by the distribution of oxyethylene groups as well as by the average mole ratio (4).

Manufacture

Ethylene oxide is produced commercially on a large scale by at least eight domestic manufacturers. Current production capacity is estimated at about 1.2 billion pounds per year (5). Nonionic surface-active agents probably consume about 120 million pounds per year with the greater proportion of the balance being consumed in the manufacture of ethylene glycol and polyethylene glycols. There are two processes commonly used in the production of ethylene oxide. About 40% of current production is made by the older chlorohydrin process and 60% by the direct catalytic oxidation of ethylene.

Ethylene oxide is a colorless gas having an ether-like odor. It condenses at low temperatures or moderate pressures into a mobile liquid having a boiling point of 51.3°F. at atmospheric pressure. It is highly flammable and can undergo exothermic reaction with itself and exothermic decomposition of its vapor. Its toxicity is of about the same order as carbon monoxide, and it can cause delayed burns on skin exposure. Rigid safety precautions must therefore be observed at all stages in its handling. Deliveries are usually made in 400-lb. drums and cylinders of smaller capacity under its own vapor pressure and in insulated tank cars under an inert atmosphere.

Most ethylene oxide condensation reactions are carried out commercially in pressure reactors at temperatures from 120° to 200°C. and pressures of 30 to 60 p.s.i.g. The reaction is exothermic to the extent of about 20 kilo calories per gram mole of ethylene oxide reacted (6). It is therefore necessary to agitate thoroughly and to control the temperature by the use of a high temperature coolant. Over-cooling can stop the reaction permitting ethylene oxide to accumulate and then suddenly react, producing an explosion. Control instrumentation of the best design and quality and a high degree of operating skill are essential.

The equipment should be constructed of materials which are nonreactive and must be thoroughly cleaned before use. Check valves in the ethylene oxide lines are necessary to prevent back flow from the reactor which can cause violent condensation in the supply tank with disastrous results. An inert gas is generally used to purge the reactor and lines of all traces of air before the addition of ethylene oxide and to serve as a blanketing atmosphere during condensation.

Although the specific steps and conditions employed in commercial operation by each manufacturer, including the Atlas Powder Company, are not generally disclosed, typical practices are described in the promotional literature of most marketers of ethylene oxide and in a number of patents. As described in one of the patents (7), a weighed charge of the selected reactant mixed with a catalyst is usually pumped from a loading tank to the reactor. Heat is then applied to bring the charge to reaction temperature, and ethylene oxide is added slowly from a weighing tank. Initiation of the reaction is indicated by a rise in temperature, and at this stage the reaction mixture may be pumped through a heat exchanger and recirculated by spraying into the upper portion or absorption zone of the reactor, which is continuously supplied with ethylene oxide vapor at a rate not exceeding its rate of consumption. By utilizing special techniques for introducing alkaline catalysts, it is possible to carry out ethylene oxide condensation with certain lipophiles, such as alkyl phenols, as a continuous operation (8).

After the addition of the desired amount of ethylene oxide, its complete reaction is indicated by a drop in pressure to a steady level. The reactor is then cooled, and the product is transferred to a treating tank where any traces of unreacted ethylene oxide can be removed by vaccum stripping. Chemical treatment to improve the color of the product or otherwise to adjust its properties may be carried out at this point. The product is then pumped through filters into a filling tank, where batch blending can be accomplished and from which it can be loaded into tank cars or drums.

The analytical control of the quality of surface-active agents produced by ethylene oxide condensation usually involves the determination of the hydroxyl value, from which the degree of oxyethylation can be calculated. Other control tests usually include pH, water content, solubility, color, and cloud-point.

General Character of Products

Since there are a number of types of lipophilic compounds in common use as sources of active hydrogen, and the degree of ethylene oxide polycondensation can be varied over a wide range, a vast number of derivatives can be produced. In most types the short-chain polyoxyethylene derivatives tend to be insoluble in water and soluble in oils. As the length of the polyoxyethylene chain is increased, water solubility increases and oil solubility diminishes. The nature of the lipophile and its linkage to the polyoxyethylene chain determines to a considerable extent the stability of the product toward various reagents and the relative performance with respect to specific application requirements.

A successful method of characterizing the general functional properties of surface-active agents has been developed by Griffin (9). Known as the hydrophile-lipophile balance or H.L.B. system, it establishes a numerical value for each surface-active agent and relates it by a scale to suitable applications. The H.L.B. number may be determined experimentally by emulsion and solubility studies, or it may be calculated by equations involving the weight percentage of oxyethylene content in polyoxyethylene surface-active agents which do not contain other oxylalkylene groups, nitrogen, or sulfur (10). A table of H.L.B. ranges and their corresponding principal applications, as reported by Griffin (11), is shown below:

H.L.B. range	*Application*
9– 6	W/O emulsifier
7– 9	Wetting agent
8–18	O/W emulsifier
13–15	Detergent
15–18	Solubilizer

The approximate relationship between H.L.B. range and water solubility, as determined by Griffin (12), is as follows:

	H.L.B. range
No dispersibility in water	1– 4
Poor dispersibility	3– 6
Milky dispersion after vigorous agitation	6– 8
Stable milky dispersion (upper end almost translucent)	8–10
From translucent to clear dispersion	10–13
Clear solution	13+

By suitable application of the H.L.B. system and an understanding of the characteristics of the available lipophiles, it becomes possible to predetermine the approximate composition of a polyoxyethylene surface-active agent intended to meet certain performance requirements.

It is estimated that about 175 million pounds of polyoxyethylene surface-active agents were produced in 1957, as compared to 50 million pounds in 1950. This substantial growth has resulted principally from their increased consumption in detergents for household use and textile mill scouring and to their application as emulsifiers in new products and processes.

Commercial Product Classes

Alkyl Phenol Ethers. One of the largest classes of polyoxyethylene surface-agents now in use is produced by the condensation of ethylene oxide with alkylphenols (13). A number of different alkylphenols can be used, but for commercial purposes diamylphenol, octylphenol, and nonylphenol are most frequently employed. These are produced by alkylating phenol with a suitable olefin, using a Friedel-Crafts type of catalyst. The hydrogen atom of the hydroxyl group on the alkylphenol enters into reaction with ethylene oxide to form a polyoxyethylene alkylphenyl ether. The ether linkage between the aromatic nucleus and the polyoxyethylene chain gives these products excellent stability to oxidizing agents and to acids and bases since it does not undergo hydrolysis.

Commercial products having from four to 30 moles of ethylene oxide condensed with a mole of alkylphenol are in widespread use. They offer a homologous series of substantially pure, colorless products having H.L.B. values from about 9 to 18. Types containing up to about 15 moles of ethylene oxide are liquids while those having higher ethylene oxide ratios are soft waxes. Although not appreciably soluble in mineral oils, products containing up to about 6 moles of ethylene oxide are soluble in aliphatic hydrocarbon solvents and insoluble in water. At mole ratios above 8 they exhibit excellent water solubility, and at all mole ratios they are soluble in carbon tetrachloride and most aromatic solvents and lower alcohols. The lower mole ratio products are used extensively as intermediates for the production of high foaming anionic detergents by sulfation of the terminal hydroxyl group. They also serve as water in oil emulsifiers for some systems and as detergents in nonaqueous media such as drycleaning solvents. In the range of 9 to 10 moles of ethylene oxide they function as outstanding aqueous detergents with relatively low foaming characteristics. Products having higher mole ratios are used as components in emulsifier compositions, as pigment dispersants, and in stabilizing latices.

Many other commercial uses based on the surface activity of this series of compounds have been found. Since they do not contain a fatty or a branched aliphatic lipophilic nucleus, they are somewhat less versatile as emulsifiers than some of the other polyoxyethylene condensates. However freedom from unethoxylated alkylphenol, their low cost, abundant availability, and excellent detergency have contributed to the leading position which they occupy. Typical commercial products of this class are represented by the "Renex 600" series of the Atlas Powder Company, the "Igepals" of the Antara Chemicals Division of General Aniline and Film Corporation, "Triton X-100" of Rohm and Haas, "Tergitol NPX" of Union Carbide Chemicals Company, "Kyro EO" of Procter and Gamble, and "Energetic W-100" of Armour and Company.

Aliphatic Alcohol Ethers. Another commercially important series of polyoxyethylene nonionic surface-active agents is produced by condensing aliphatic alcohols containing from 12 to 18 carbon atoms with ethylene oxide to form polyoxyethylene alkyl ethers (14). These products are chemically similar to the polyoxyethylene alkylphenol ethers but differ from them in some of their functional properties because of the nature of the lipophiles. The principal alcohols used in making these surface-active agents include the naturally derived fatty and resin alcohols, synthetic lipophilic alcohols, and hydrophilic polyhydric alcohols.

The lipophilic alcohols derived from natural fats and oils were among the first materials used in making nonionic polyoxyethylene surface-active agents, and they continue to represent the largest segment of the aliphatic polyether class. These alcohols are made from fatty esters by sodium reduction or by catalytic hydrogenation. The fatty alcohols used most extensively in producing aliphatic polyoxyethylene ethers are lauryl, oleyl, tallow, cetyl, and hydroabietyl.

A number of synthetic lipophilic alcohols are produced commercially and are used in making alphatic polyoxyethylene ethers. Trimethyl nonanol and certain of the branched chain alcohols formed by the Oxo process are the most important of this class. Tridecyl alcohol is the most widely used Oxo alcohol, and its branched chain polyoxyethylene ethers are being used in increasing amounts because of their valuable detergent, foaming, and wetting properties.

As in the case of the polyoxyethylene alkylphenol ethers, the aliphatic polyoxyethylene ethers exhibit excellent stability to acids and bases. The condensation of from 1 to 5 moles of ethylene oxide with a higher aliphatic alcohol usually gives products which are insoluble in water and are more soluble in oils than the alkylphenol ethers. Products of this type are useful as water in oil emulsifiers and are often used as intermediates for the production of valuable anionic detergents by sulfation for use in liquid dishwashing products and shampoos. The foaming properties of some of the polyoxyethylene aliphatic ethers are relatively good for nonionics. While most of these products are liquids, it is possible to obtain waxes by the addition of sufficient ethylene oxide, but this usually results in H.L.B. values well above the optimum for detergency.

Among the more important uses in which polyoxyethylene alkyl ethers are often preferred to other surface-active agents are raw wool scouring, dye leveling, liquid dishwashing detergents, improving the regenerative spinning of viscose fibers, kier boiling of cotton, mold release lubricants, detergent sanitizers, alkaline metal cleaners, secondary recovery in oil wells, and foaming agents for air drilling and as emulsifiers for a variety of materials, including silicones and polyethylene.

Typical commercial polyoxyethylene alkyl ether products are represented by the "Brij" and "Renex 30" series of the Atlas Powder Company, "Sterox AJ" of Monsanto Chemical Company, "Peregal O" of the Antara Division of General Aniline and Film Corporation, and the "Poly-Tergent J" series of the Olin-Mathieson Chemical Corporation.

Aliphatic Ether Esters. Closely related to polyoxyethylene alkyl ethers is a class of products identified as polyoxyethylene ether esters. These compounds are formed by partially esterifying a polyhydric alcohol, such as sorbitol, with a fatty acid, leaving at least one hydroxyl group unesterified and then condensing the unesterified hydroxyl groups with ethylene oxide. Products of this type are represented by the "Tweens," which were first introduced commercially in 1940 by the Atlas Powder Company and have been used in increasingly greater volume each year as emulsifiers and as textile lubricants and antistatic agents. In the step of partial esterification, sorbitol undergoes anhydrization to form a mixture of anhydrosorbitols which contain one or two inner ether linkages and either two or four hydroxyl groups that are partially esterified. Ether esters are also produced by Atlas by first condensing ethylene oxide with one or more of the six hydroxyl groups of sorbitol and subsequently esterifying this compound with a fatty acid. By this process, anhydrization of the sorbitol is avoided, and a somewhat different structure is obtained.

The ether esters do not possess complete stability to hydrolysis in strongly acid or basic media because of the ester linkage joining the lipophile to the hydrophile. The polyol portion of these compounds constitutes part of the hydrophilic component along with the oxyethylene groups and permits the incorporation of a number and a variety of lipophilic groups, resulting in a very wide range of properties. The complex structure of the ether esters enables them to perform many emulsification and textile lubricating operations that cannot be accomplished as satisfactorily by other polyoxyethylene surface-active agents. The exceptionally good color and odor of the ether esters has resulted in their extensive use in cosmetic and pharmaceutical preparations. Their high emulsifying efficiency accounts for their preference in a number of large-volume applications, such as formulating agricultural pesticide emulsions and oil-well drilling muds.

Polyoxyethylene Esters. Probably about equal in volume of consumption to polyoxyethylene alkylphenol ethers are the polyoxyethylene esters. These products are usually made by the condensation of ethylene oxide with the carboxyl hydrogen of a carboxylic acid. They can also be produced by esterifying such an acid with a polyethylene glycol formed by condensing ethylene glycol with ethylene oxide. Monoesters are formed by condensing ethylene oxide directly with a carboxylic acid, and diesters are produced by further esterification, involving the hydroxyl group at the end of the polyoxyethylene chain. Either mono or diesters can also be formed by esterifying one or both of the hydroxyls of a polyethylene glycol. The polyoxyethylene monoesters can be sulfated at the hydroxyl group to give anionic compounds.

The ester structure of these surface-active agents makes them generally unsuitable for use in strongly acid or alkaline solutions because of its tendency to hydrolyze. However the relatively low cost of a number of carboxylic acids makes them attractive as raw materials where the products are to be used in the absence of strong acids or bases at elevated temperatures.

The principal carboxylic acids used in the commercial manufacture of polyoxyethylene ester condensates are the fatty acids, rosin acids, and naphthenic acids. Products made from the fatty acids are used commercially as emulsifiers and as textile lubricants. Refined tall oils containing various percentages of fatty and rosin acids are the chief source of polyoxyethylene esters (15). The rosin acid esters are appreciably more resistant to hydrolysis by alkalis than are the fatty acid esters and will withstand mild oxidixing agents. Consequently the tall oil esters are used extensively as detergents with alkaline builders for both household and commercial laundering and for textile mill scouring. From 12 to 16 moles of ethylene oxide are usually condensed with tall oil to produce detergents. These products are viscous liquids which can be incorporated in satisfactory proportions with solid ingredients in making powdered cleaners. By mixing them with approximately equal weight proportions of urea, solid granular compositions are produced (16).

The foaming properties of the polyoxyethylene tall oils are quite low, which makes them adaptable to mechanical washing operations where strong agitation is encountered. They also exhibit good tolerance to metallic ions found in hard water and consequently can be used in detergent products distributed on a nation-wide basis.

Among the polyoxyethylene ester class of surface-active agents, the fatty acid ester types are represented by the "Myrj" series of the Atlas Powder Company and the "Ethofats" of Armour and Company. Typical commercial polyoxyethylene tall oil esters are the "Renex 20" series of the Atlas Powder Co., "Sterox CD" of Monsanto Chemical Company, "Teox 120" of the Blockson Chemical Division of Olin Mathieson, and the "Energetics" of Armour and Company. Products sold under the name of "Victamul" by the Victor Chemical Works are polyoxyethylene higher alkyl phosphate derivatives which also contain the ester linkage.

Polyoxyethylene Alkyl Amides. Polyoxyethylene surface-active agents derived from lipophiles in which the active hydrogen is attached to nitrogen form an important commercial class. Ethylene oxide can be condensed with each of the two hydrogens in a higher alkyl amide to form N,N-substituted polyoxyethylene acid amides. These products are similar to the polyoxyethylene esters in their physical properties but are generally more resistant to hydrolysis. They are used principally as emulsifiers and are frequently combined with other nonionic surface-active agents or with anionics to obtain the desired performance in specialized applications. Typical commercial products of this class are the "Ethomids" of Armour and Company.

Polyoxyethylene Alkyl Amines. Another widely used class of nitrogen-based polyoxyethylene surface-active agents is represented by the compounds obtained by the condensation of higher alkyl amines with ethylene oxide (17). Either primary or secondary substituted amines are formed in this manner, depending on whether one or both of the available hydrogens are condensed with ethylene oxide. The most distinguishing chemical characteristics of the polyoxyethylene alkyl amines are their cationic properties and their ability to form salts with acids in a manner similar to the alkyl amines themselves. As the number of moles of condensed ethylene oxide is increased, the cation activity of these compounds diminishes and they become more like nonionic compounds in their behavior toward anions. Like most of the other polyoxyethylene condensates, products containing relatively low mole ratios of oxyethylene groups to the alkyl group are liquids whereas solids are obtained at ratios above about 50 to 1. Water solubility generally is obtained at a mole ratio of around 5 to 1, and typical inverse solubility with respect to temperature is exhibited. Because of their ability to form salts, their aqueous solubility in the presence of low molecular weight acids is generally greater than other polyoxyethylene alkyl condensates of equivalent oxyethylene mole ratios and the corresponding hydrocarbon solubility is greater in the presence of high-molecular-weight organic acids.

The alkyl amines most widely used in the preparation of commercial polyoxyethylene condensates are the primary fatty amines and dehydroabietyl amine derived from rosin. The nature of the alkyl amine has considerable influence on the physical and functional properties of the polyoxyethylene derivatives. Branched-chain alkyl groups have been found to induce properties different from the straight-chain alkyls, and differences in properties between the derivatives of saturated and unsaturated alkyl groups occur.

The cationic properties of the polyoxyethylene alkyl amines results in their preferential adsorption on negatively charged surfaces, such as cellulosic and certain synthetic textile fibers, vitreous products, and most metals. In the textile field this has made possible the substantive attachment of fatty radicles to fibers to impart very desirable lubricating and softening properties and beneficially to alter the cross-sectional configuration in the regenerative spinning of viscose rayon fibers. Most of the cationic compounds of this type also exhibit pronounced antistatic characteristics. On vitreous surfaces, such as glass, they offer one of the mechanisms of obtaining a substantial degree of adsorptive adhesion. Their strong affinity for ferrous metal surfaces makes them valuable in the formulation of the filming type of corrosion inhibitors. Some bactericidal properties are also exhibited by these cationics.

Among the commercial compounds of the polyoxyethylene alkyl amine class, typical products are "G-3780" and the "Cronox 600" series of the Atlas Powder Company, the "Ethomeens" of Armour and Company, and the "Priminox" series of Rohm and Haas. Polyoxyethylene dehydroabietyl amines are marketed under the name of "Polyrad" by the Hercules Powder Company.

Polyoxyethylene Thioethers. Another commercially important class of nonionic surface-active agents is produced from lipophiles in which the active hydrogen is attached to sulfur. These products are made by the condensation of alkyl mercaptans with ethyllene oxide to form polyoxyethylene thioethers (18). Their chemical configuration is similar to the polyoxyethylene alkylphenol and alkyl ethers but differs in the presence of sulfur rather than oxygen as the link between the lipophile and the polyoxyethylene chain.

The outstanding characteristic of the polyoxyethylene thioethers is their instability to oxidizing agents. Although this precludes their use in some applications, it is a distinct advantage where conditions require the inactivation of a surface-active agent in a process. They exhibit a fair degree of stability to nonoxidizing acids and excellent stability to alkalis.

The alkyl mercaptans usually employed for condensation with ethylene oxide are of the C_{10} to C_{18} branched-chain types made from olefin polymers. These mercaptans are established commercial products, which are normally in good supply. Condensation with ethylene oxide proceeds in much the same manner as it does with other compounds containing active hydrogen.

In neutral or alkaline solutions the performance of the polyoxyethylene thioethers qualifies them for competition with other polyoxyethylene ethers and, as in the case of most of the other individual products, certain applications have been found where they are preferred. Commercial uses include emulsifiers, detergent sanitizers, and dairy cleaners. Their inactivation by oxidizing agents can be utilized in reducing stream pollution and in destroying re-wetting action where this is desirable.

Typical commercial products representing the polyoxyethylene thioether class are "Nonic 218," "Nonic 234," "Nonic 258," and "Nonic 260" produced by Pennsalt Chemicals Corporation and "Sterox SE," "Sterox SK," "Sterox No. 5," and "Sterox No. 6" made by Monsanto Chemical Company.

Polyoxyalkylene Block Polymers. An interesting and commercially important class of polyoxyethylene derivatives is produced by using polyoxypropylene glycol as the source of active hydrogen for condensation with ethylene oxide (19). Propylene oxide is similar to ethylene oxide, but the oxypropylene units formed by its polycondensation are more lipophilic than oxyethylene units. By controlling the degree of propylene oxide condensation, it is possible to produce a series of polypropylene glycol lipophiles having a fairly wide range of properties. Ethylene oxide can then be condensed with the hydroxyl groups at each end of these polypropylene glycol blocks to form an almost infinite number of hydrophile-lipophile combinations. The Wyandotte Chemicals Corporation produces surface-active agents of this type under the name "Pluronic." Polypropylene glycols having molecular weights of from 800 to 2,500 are employed in these commercial products, and a useful graphic relationship between the molecular weight of the lipophile and the percentage of condensed ethylene oxide has been established to assist in selecting products to accomplish specific functions.

A modification of the above type of so-called block polymer surface-active agents is produced by condensing propylene oxide with a monofunctional alcohol. In this manner only one site becomes available for the condensation of ethylene oxide on the polyoxypropylene chain. Block polymers are also made in a similar manner by condensing propylene oxide with each of the four available hydrogen atoms of ethylenediamine to form a branched lipophilic block with which ethylene oxide is then condensed to produce surface-active agents. The Wyandotte "Tetronic" series consists of products of this type.

The properties of the block polymer surface-active agents make them useful where low foam and good dispersing action are required. The solid consistency of some of the high molecular weight products which are available in flake form makes them particularly adaptable to dry formulation.

Summary

A limited presentation has been made in the preceding discussion of some of the more important aspects of ethylene oxide condensation with respect to surface-active agents. As a commercial process it is an economical means of introducing hydrophilic ethoxy groups to achieve the desired balance with lipophiles. The hydrophilic characteristics of ethoxy groups result from hydration of ether-linked oxygen atoms. The condensation of ethylene oxide with compounds having active hydrogen atoms is carried out commercially at moderate temperatures and pressures in the presence of catalysts with careful regard to safe operating procedures. Nonionic agents having a variety of properties and uses are formed by condensing ethylene oxide with alkyl phenols, higher aliphatic alcohols, polyhydric alcohol partial esters, carboxylic acids, higher alkyl amides, alkyl mercaptans, and polypropylene glycols. Condensation of ethylene oxide with higher alkyl amines yields cationic agents.

In recent years a considerable volume of literature has been published on the subject of ethylene oxide and nonionic surface-active agents. The references cited should serve as a source of more complete and detailed information.

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