figure may be higher depending on the efficiency of the operation.

Properties of oils and fats are dependent not only on the degree of sulfation but on the soap content as well. Therefore, in evaluating all sulfated oils, attention should be given to the ratio between total alkali and free fatty acids, as well as to the combined SO_3 values.

It is only natural that over the years the products produced by sulfation with commercial sulfuric acid would not fill all requirements, and so many attempts have been made to increase the degree of sulfation. It was early recognized that the water of reaction was one factor working against the production of high sulfations. Logically the search for stronger reagents turned to 98% sulfuric acid, fuming sulfuric acid, chlorosulfonic acid, and the like. In recent years liquid sulfur trioxide has received considerable attention. All of these have been used in various amounts, sometimes to excess, but some have tended to give sulfonation reaction products rather than higher sulfations. This holds true in most cases for the various solvents used as diluents as well as for such dehydrating agents as acetic anhydride. Sulfonation with these stronger agents is much more rapid and requires, for the most part, positive means of control.

Gilbert and Jones (2) have made a careful survey of sulfonation and sulfation and of the various reagents in use. Gilbert and co-workers (3) in their work with liquid sulfur trioxide have described action of this material on long-chain saturated acids as developed by Stirton and co-workers (7). They have prepared disodium a-sulfopalmitate as an example in which the properties of the carboxyl group have been modified by the introduction of an adjacent, solubilizing sulfonic acid group. There is a technical brochure available (10) describing the properties and potential uses of such a product. Stirton and co-workers have also prepared sodium oleyl sulfate as an example in which the carboxyl group is replaced by the $-CH_2OSO_3Na$ group. By special treatment they have left the unsaturated bonds untouched, and so a whole new field for investigation opens.

Not to be neglected is mention of Sunderland (8), who in 1935 published a discussion of the mechanism of sulfation, cited various examples of the process, and listed many of the uses of sulfated oils at that time. These uses are many and varied. The textile, tanning, and paper industries are large consumers. They are used as defoamers, specialized detergent wetting agents, emulsifiers and softeners, as flotation agents, the manufacture of inks, dyestuffs, and even as lubricants. The list is almost endless and, in conjunction with other surface-active agents, promises to become longer. Although thousands of surface-active agents, emulsifiers, and related products (11) are now available, the sulfated oils still enjoy a steady market due in part to their inherent properties, and in part to their economic position.

REFERENCES

1. Burton, D., and Robertshaw, G. F., "Sulfated Oils and Allied Products," ch. 2 & 3, New York Chemical Publishing Co., 1940.
2. Gilbert, E. E., and Jones, E. P., Ind. and Eng. Chem., *43*, 2022 (1951).
3. Gilbert, E. E., Veldhuis, B., Carlson, E. J., and Giolito, S. L., Ind. and Eng. Chem., *45*, 2065 (1953).
4. Hart, R., Ind. and Eng. Chem., Anal. Ed., 7, 135 (1935).
5. Koppenhoefer, R. M., J. Am. Leather Chem. Asso., *34*, 622 (1939).
6. Loffl, K., Seifenfabrikant, *40*, 81–83 (1920).
7. Stirton, A. J., Weil, J. K., Stawitzke, Anna A., and James, S., J. Am. Oil Chemists' Soc., *29*, 198–201 (1952).
8. Sunderland, A. E., "Sulfonated Oils," Soap, Oct., pp. 61–71; Nov., pp. 61–64; Dec., pp. 67–69 (1935).
9. Rueggeberg, W. H. C., and Sauls, T. W. (to Tennessee Corp.), U. S. Patent 2,743,288 (Apr. 24, 1956).
10. Technical Brochure, Armour Chemical Division Bulletin G-7 (1956).
11. Technical Brochure, "Classification and Identification Dissertation on Surface-Active Agents," Aquaness Corp.
12. Twitchell, Ernst, U. S. Patent 628,503, July 11, 1899.

RECOMMENDED READING

Schwartz-Perry, "Surface-Active Agents," Interscience Publishers, New York, 1949.

Ralston, A. W., "Fatty Acids and Their Derivatives," John Wiley and Sons, New York, 1948.

Groggins, P. H., "Unit Processes in Organic Synthesis," McGraw-Hill Book Co., New York, 1952.

Production of Alkylene Oxide Derivatives

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Although the products are comparatively new, the production of alkylene oxide derivatives is becoming an increasingly important unit process in the detergent industry. According to the last U. S. Tariff Commission Report, the production of non-ionic detergents was 130 million lbs. in 1954 (1), and it is estimated that more than 160 million lbs. will be produced this year. The majority of these are derivatives of ethylene oxide, which accordingly will receive the most emphasis in this discussion. In general, the same reaction conditions employed for the production of ethylene oxide derivatives can be applied to the other alkylene oxides, of which propylene oxide is the next most important. This discussion will be limited to those reactions which directly involve the alkylene oxides, but it should be recalled that many alkylene oxide derivatives are produced by esterification of fatty acids with polyalkylene glycols, which in turn are derivatives of alkylene oxide and water.

Nature of the Reaction

The increasing popularity of alkylene oxide derivatives in the surface-active field is based on the fact that practically any hydrophobe-hydrophile balance can be obtained by varying the ratio of the reactants. Thus the products can be tailor-made for optimum detergency, wetting, lime-soap dispersion, emulsifying properties, etc., as desired. This is done by reacting a hydrophobic compound, such as an alkylphenol, a fatty acid, a fatty alcohol, or other like compound which contains a reactive hydrogen, with the proper proportion of ethylene oxide (2, 3). For typical non-ionic detergents this proportion is about two parts by weight of ethylene oxide for one part of the hydrophobic compound.

As illustrated by the equations,

$$(1)\quad ROH + C_2H_4O \longrightarrow ROC_2H_4OH$$

$$(2)\quad ROC_2H_4OH + C_2H_4O \rightarrow ROC_2H_4OC_2H_4OH$$

$$(3)\quad ROH + n\,C_2H_4O \longrightarrow RO(C_2H_4O)_nH$$

the first mole of ethylene oxide reacts with the reactive hydrogen of the hydrophobic compound (in this case, a fatty alcohol) to give a primary reaction product which contains a newly-formed reactive hydrogen ($-C_2H_4OH$) that can react with another mole of ethylene oxide. This process may be repeated to build long hydrophilic polyoxyethylene chains, which can contain as many as a hundred oxyethylene units. The principal non-ionics contain six to 15 oxyethylene units.

Incidentally it should be understood that these alkylene oxide derivatives are not single compounds but are very complex mixtures. Thus the stated number of oxyethylene units represents only an average figure and includes products with polyoxyethylene chains which are smaller and larger than indicated by the value of n. The composition of the mixtures follows a statistical distribution which may be calculated by Poisson's formula (4). Several years ago Mayhew and Hyatt showed by the molecular distillation of nonylphenol-ethylene oxide adducts that the composition of these products was about the same as calculated by Poisson's formula (5). For some purposes it would be desirable to obtain a narrower distribution than that given by Poisson's formula. To the writer's knowledge, this has not been attained although it is not difficult to obtain the opposite result, namely, to get a wider distribution than the calculated one!

Reaction Conditions

As shown above, the preparation of alkylene oxide-based detergents involves the formation of long polyoxyalkylene chains. In practice this is accomplished as suggested by the above equations, by the gradual stepwise addition of the alkylene oxide. Briefly the hydrophobic compound plus catalyst is heated to the desired reaction temperature, and the alkylene oxide is then added gradually no faster than it reacts until the proper oxide to hydrophobe ratio has been reached. The primary advantage of this procedure is its inherent safeness. Alternate procedures which involve mixing large proportions of the alkylene oxides with the other component and catalyst can only be carried out on a very small scale or in a continuous operation. This is because the reaction is highly exothermic; about 20 kg. cal. is liberated for each mole of ethylene oxide reacted. Thus on a production scale it is essential that adequate cooling be provided and that large amounts of unreacted oxide not be permitted to accumulate in the reactor.

In this connection it is desirable to note additional precautions which should be observed in handling the alkylene oxides. These materials are hazardous because they are highly flammable, they can form explosive mixtures with air, their auto-polymerization can be violent, and they are moderately toxic. These properties make it mandatory that these materials be protected against ignition, heat, air, and contamination. In general, this means that the oxides should be stored and used in proper containers purged with an inert gas, such as nitrogen. Specific suggestions on this subject may be found in a chemical safety data sheet issued by the Manufacturing Chemists' Association (6). Provided that the hazardous nature of these materials is recognized and respected, the manufacture of alkylene oxide derivatives can be a safe operation as attested by the excellent safety record of the producers in this country.

Temperature. The reaction temperature depends on the other reaction variables and the nature of the starting material. The reaction is impractically slow however unless elevated temperatures are used. In the presence of the usual alkaline catalyst the range 120 to 200°C. covers practically all reactions, with the majority being carried out at 150 to 180°C. If an acidic type catalyst, such as boron trifluoride, is used, the reaction may be carried out at lower temperatures, for example, 50–75°C.

Pressure. Generally all oxyalkylation reactions are carried out in the plant under pressure. This is desirable in order to maintain a reasonably high concentration of the alkylene oxide in the hot reaction mixture and thereby shorten the reaction time. The pressure need not be high. The range 10 to 200 psig. will cover most cases, with the narrower range 20 to 50 psig. being preferred. The reaction can be carried out at atmospheric pressure in ordinary glass equipment in the laboratory at the expense of longer reaction times. The convenience of this procedure was used by Karabinos and his co-workers to prepare a variety of non-ionics for detergency studies (7-11).

Catalysts. A catalyst is necessary in almost all cases because otherwise the reaction rate is too slow, even at 200°C. Most reactions are run in the presence of an alkaline catalyst, which is usually sodium hydroxide. Other alkaline catalysts which can be used include sodium methoxide, potassium hydroxide, potassium carbonate, sodium metal, and sodium acetate. Only a small amount of catalyst is required; the usual range is one-tenth to 1% of the weight of the starting material.

Acidic catalysts, such as boron trifluoride (12) and acid clays (13), have also been used to produce alkylene oxide derivatives but are less frequently used than alkaline catalysts. As noted above, lower temperatures may be employed when these acidic catalysts are used and the reaction products are generally lighter-colored than similar products produced by alkaline catalysts. The acidic catalysts promote undesirable side-reactions however so that as much as 10 to 20% of the oxide introduced may be converted to by-products such as dioxane, dioxolanes, etc. Accordingly the acidic catalysts are rarely used.

Reaction Procedure

As indicated above, most alkylene oxide derivatives are produced by batch operations. To illustrate the procedure a typical run is described as follows:

The reactor (Figure 1) is charged with a mixture of 1,350 lbs. of d.p. stearic acid and 2.7 lbs. of flaked sodium hydroxide. The reactor is evacuated and purged with nitrogen twice and the contents heated with stirring to 150°C. A final evacuation reduces the pressure in the reactor to about 20 mm. of mercury. Liquid ethylene oxide is then forced by nitrogen pressure (the nitrogen pressure on the ethylene oxide storage is held at about 75 psig.) until the pressure in the reactor rises to about 10 psig. The flow of ethylene oxide is then cut off until the pressure in the reactor drops. This is to insure that the reaction starts and to prevent any build-up of unreacted ethylene oxide in the reactor. Note that the ethylene oxide storage is protected by a series of check valves. Although this precaution is mandatory, check valves can fail. Accordingly it is essential that the pressure in the reactor never be allowed to exceed the pressure on the ethylene oxide storage. Should this occur in conjunction with check valve failure, the oxide storage may become contaminated with possibly disastrous results. This potential hazard can be practically eliminated by feeding the oxide into the vapor phase at some sacrifice of reaction rate.

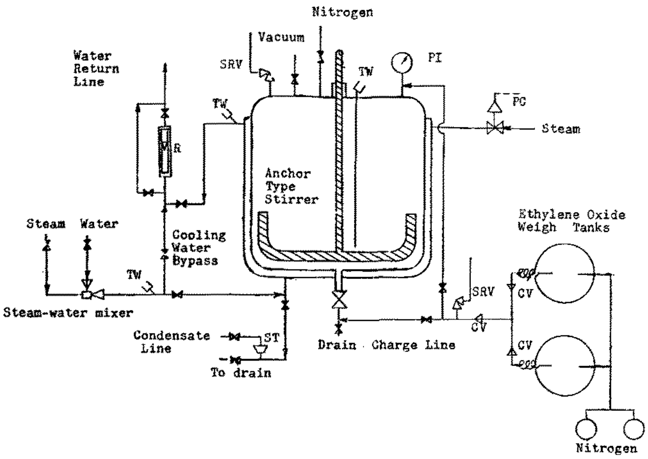


FIG. 1. Batch Ethoxylation Unit.

CV	Check valve	SRV	Safety relief valve
PC	Pressure-controller	ST	Steam trap
PI	Pressure gauge	TW	Thermowell
R	Rotameter		

After the reaction starts, the pressure in the reactor will drop and the reaction temperature will tend to rise. The flow of cooling water is then started, and the pressure in the reactor is brought back to 10 psig. by the addition of more oxide. As the reaction is brought under control, the reaction temperature and pressure are raised gradually to the working range of 170–180°C. at 35–40 psig. In a number of cases an induction period is encountered in which the reaction rate will be found very slow. Then, generally after one mole of alkylene oxide has reacted with the reactive hydrogen compound, the reaction will proceed at a much faster rate at the same temperature and pressure. In the present example a period of about 1 hr. is required to add the first 200 lbs. of ethylene oxide; the remaining 2,000 lbs. are added in the next four hours to produce a stearic acid-ten mole ethylene oxide adduct. At the end of the run, after the oxide flow has been discontinued, the pressure in the reactor will drop to below 0 psig. The reaction mixture is then cooled, decolorized if desired, and discharged. A particularly attractive feature about this operation is that the yield is quantitative.

Alkylene oxide derivatives can be produced also by continuous procedures, but little detailed information on successful operations is available. It would appear simple to force a mixture of the alkylene oxide, reactive hydrogen compound, and catalyst through suitable heat exchangers and remove a finished product at the other end, but such is not the case. It is not easy to keep the reaction under control, and the products tend to have a broader distribution than similar products prepared by batch methods. The larger the proportion of alkylene oxide required, the more difficult the problem becomes. Accordingly it is not general practice to produce non-ionic detergents of this type by continuous methods.

Equipment

The equipment employed for the batch production of alkylene oxide derivatives is essentially an autoclave designed to operate at about 50 psig. It must be equipped with heat exchangers and mixing means. These may be internal or external or both. Commonly the vessels are jacketed and may be heated or cooled by this means, perhaps in combination with internal coils. External heat-exchangers may also be used; the reaction mixture is circulated by an external pump. The latter also provides mixing, but generally some type of internal stirrer is used for good mixing is very important. The seal at the stirrer shaft can be a source of trouble, but packings based on mixtures of Teflon and asbestos have given reasonably good service.

The alkylene oxides can be stored and piped in ordinary iron equipment, but stainless steel is the preferred material of construction for the usual batch-reactor. Glass-lined and enameled vessels may also be used satisfactorily. In those cases in which the color of the product is not as important as economy, iron equipment can be used. Indeed, for the semi-continuous production of one particular product, an iron vessel may give very satisfactory results as its surface becomes passivated. But for the general purpose unit which must be cleaned frequently because it is required for the production of many different products, including fatty acid derivatives, it is difficult to find an equal to stainless steel.

Types of Products

Now that we have outlined the nature of the reaction, the reaction variables, the procedure, and the equipment, it might be well to consider briefly the various types of alkylene oxide derivatives which are most commonly produced.

Water Derivatives.

$$HOH + nC_2H_4O \longrightarrow HO(C_2H_4O)_nH$$

The first members of this series, ethylene glycol, propylene glycol, and their di- and tri- derivatives, are produced by the reaction of the alkylene oxides with water in a continuous operation on a tremendous scale. The production of these materials and the glycol ethers and ethanolamines must be considered as outside the scope of this discussion. The higher polyoxyalkylene glycols however are produced by the procedures described above. Ethylene glycol or diethylene glycol is charged to the reactor with a trace of caustic catalyst, and ethylene oxide is added until the molecular weight has been increased to 300, 400, 600, or 1,000 as desired. At the end of the reaction the catalyst is neutralized, and the product is decolorized, if necessary, and filtered. If a higher polyethylene glycol, such as polyethylene glycol of average molecular weight 6,000, is wanted, then the charge would most likely be polyethylene glycol 1,000 for the equivalent amount of diethylene glycol would scarcely wet the bottom of the reactor.

Alcohol Derivatives.

$$ROH + nC_2H_4O \longrightarrow RO(C_2H_4O)_nH$$

The recent availability on a commercial scale of the higher fatty alcohols (14, 15) and tridecyl alcohol has resulted in considerable interest in their ethylene oxide derivatives. Not only are these derivatives being used as non-ionic detergents, but their lower ethylene oxide adducts are also being employed as intermediates for anionic surfactants. Thus

$$ROC_2H_4OC_2H_4OC_2H_4OH \xrightarrow[NaOH]{SO_3} ROC_2H_4OC_2H_4OC_2H_4OSO_3Na$$

It has been found that the addition of three to five moles of ethylene oxide to a long chain alcohol will give an alcohol whose sulfate has improved foaming and solubility properties. The preparation of the ethylene oxide adducts is accomplished readily without complication.

Mercaptan Derivatives.

$$RSH + C_2H_4O \longrightarrow RSC_2H_4OH$$
$$RSC_2H_4OH + nC_2H_4O \longrightarrow RS(C_2H_4O)_{n+1}H$$

Long-chain mercaptans can be prepared by the addition of hydrogen sulfide to olefins. The conversion of these materials into polyoxyethylene thioethers is carried out in the usual manner in the presence of an alkaline catalyst. It is of interest to note that the first mole of ethylene oxide can be added selectively to a mercaptan to obtain the thioglycol ether, RSC_2H_4OH. The addition of more oxide then follows Poisson's distribution formula.

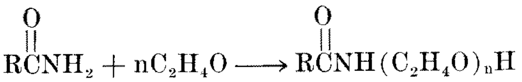
Alkylphenol Derivatives. In the same manner the alkylene oxides can also be added selectively to phenols to obtain the monoalkylene glycol arylethers. Again, after the first mole of oxide has added, the preparation of the higher adducts proceeds according to Poisson's distribution to give a spectrum of products. Octylphenol and nonylphenol, which may be prepared by the alkylation of phenol with diisobutylene and propylene trimer, respectively, are the most important alkylphenols used. The ethylene oxide adducts in the range six to 15 ethylene oxide units are excellent emulsifiers, wetting agents, and detergents. Their outstanding stability and compatibility with other surfactants has made these non-ionics very popular for industrial as well as household applications. Incidentally it should be noted that the sulfate of the nonylphenol-4 EO adduct is an excellent base for liquid dish-washing detergents because of its superior foaming properties.

Amine Derivatives.

$$RNH_2 + C_2H_4O \longrightarrow RNHC_2H_4OH$$
$$RNHC_2H_4OH + C_2H_4O \longrightarrow RN(C_2H_4OH)_2$$
$$RN(C_2H_4OH)_2 + nC_2H_4O \longrightarrow RN(C_2H_4O)_{n+2}H_2$$

The reaction of alkylene oxides with long-chain amines is more complicated than the preceding cases. As illustrated, both reactive hydrogens of primary fatty amines are substituted before much polyoxyalkylation occurs. In many cases the basic nature of the starting material provides sufficient catalyst for the reaction. It is noted however that additional catalyst (for example, sodium hydroxide or potassium hydroxide) may be found advantageous either to accelerate the reaction or to modify the distribution of products. In the latter respect the reaction temperature is likely to prove a more important factor than in the earlier examples.

Amide Derivatives.

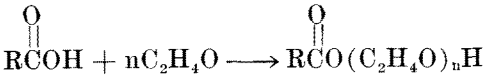


$$R\overset{O}{\overset{\|}{C}}NH_2 + nC_2H_4O \longrightarrow R\overset{O}{\overset{\|}{C}}NH(C_2H_4O)_nH$$

Fatty acid amides require an alkaline catalyst in order to react with alkylene oxides at reasonable rates and temperatures. The possibility exists that the second hydrogen on the amide is sufficiently reactive to give disubstituted derivatives, but it is believed that the main reaction is substantially as shown.

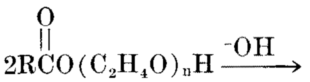
Fatty Acid Derivatives.

1.



$$R\overset{O}{\overset{\|}{C}}OH + nC_2H_4O \longrightarrow R\overset{O}{\overset{\|}{C}}O(C_2H_4O)_nH$$

2.



$$2R\overset{O}{\overset{\|}{C}}O(C_2H_4O)_nH \xrightarrow{^-OH} R\overset{O}{\overset{\|}{C}}(C_2H_4O)_n\overset{O}{\overset{\|}{C}}R + HO(C_2H_4O)_nH$$

Although many have the impression that alkylene oxides add to fatty acids to produce polyalkylene glycol monoesters, as shown by equation 1, such is not the case. Instead, in the presence of the usual alkaline catalyst, transesterification reactions occur as indicated by equation 2. As a result, the fatty acid-alkylene oxide adducts are mixtures of polyalkylene glycols, polyalkylene glycol monoesters, and polyalkylene glycol diesters. It has been found (16) that the composition of such products is similar to the mixture obtained by the esterification of a polyalkylene glycol with one mole of fatty acid.

Mixed Alkylene Oxide Derivatives. Several years ago it was shown (17) that a long polyoxypropylene chain could be used as the hydrophobic portion of a surface-active agent in combination with hydrophilic polyoxyethylene groups. Since that time these products have found many uses. The versatility of the reaction by which these materials are produced is especially noteworthy. The surfactant manufacturer can now vary the size of the hydrophobic group at will as he is no longer limited to the former customary range of eight to 18 carbon atoms in the hydrophobic chain.

Miscellaneous Derivatives. In addition to the above classes of alkylene oxide derivatives, there are a number of technically important products which should be mentioned. These include alkylene oxide deerivatives of sorbitol esters, lanolin, beeswax, tall oil, rosin acids, and a variety of glycerides. With few exceptions all of these are produced by the procedure given above.

Summary

In this discussion we have reviewed the production of alkylene oxide derivatives which are becoming increasingly important surfactants. The process has been shown to be comparatively simple although the products are very complex mixtures. The course of the reaction has been indicated for the most important types of products and the reaction variables discussed.

Perhaps the only disadvantage of this unit process is the hazardous nature of the alkylene oxides. These can be handled safely however, as proven by the safety record of the current producers.

REFERENCES

1. U. S. Tariff Commission, Washington 25, D. C., Rept. Synthetic Organic Chemicals, 1954.
2. Schoeller, C., and Wittwer, M. (to I. G. Farbenindustrie), U. S. Patent 1,970,578 (August 21, 1934).
3. Steindorff, A., Balle, G., Horst, K., and Michel, R. (to General Aniline and Film Corp.) U. S. Patent 2,213,477 (Sept. 3, 1940).
4. Flory, P. J., J. Am. Chem. Soc., *62*, 1561 (1940).
5. Mayhew, R. L., and Hyatt, R. C., J. Am. Oil Chemists' Soc., *29*, 357 (1952).
6. Manufacturing Chemists Association Inc., Washington, D. C., "Chemical Safety Data Sheet SD-38, Ethylene Oxide," February 1951.
7. Stoltz, E. M., Ballun, A. T., Ferlin, H. J., and Karabinos, J. V., J. Am. Oil Chemists' Soc., *30*, 271 (1953).
8. Ballun, A. T., Schumacher, J. N., Kapella, G. E., and Karabinos, J. V., *ibid.*, *31*, 20 (1954).
9. Karabinos, J. V., and Ballun, A. T., *ibid.*, *31*, 136 (1954).
10. Kapella, G. E., Bartels, G. E., Ballun, A. T., and Karabinos, J. V., *ibid.*, *31*, 392 (1954).
11. Karabinos, J. V., Bartels, G. E., and Kapella, G. E., *ibid.*, *31*, 419 (1954).
12. Toussaint, W. J., (to Carbide and Carbon Chemicals Corp.) U. S. Patent 2,293,868 (August 25, 1942).
13. Dehnert, H., and Krey, W. (to I. G. Farbenindustrie) U. S. Patent 1,996,003 (March 26, 1935).
14. Hill, E. F., Wilson, G. R., and Steinle, E. C., Ind. and Eng. Chem., *46*, 1917 (1954).
15. Chemical Week, *76*, 20 (June 18, 1955).
16. Unpublished data, Jefferson Chemical Company Inc.
17. Vaughn, T. H., Jackson, D. R., and Lundsted, L. G., J. Am. Oil Chemists' Soc., *29*, 240 (1952).