To obtain the most efficient reaction it is important that the quantities of materials be carefully measured, and this is most readily accomplished in a batch operation by weighing all of the feed streams which enter into the reaction. The inert solvent may be measured volumetrically as small variations in the concentration of this material will not affect the reaction for any particular oil. However it is necessary to vary the amount of inert solvent used for different oils so that fluidity is maintained in the reactor. The sodium is weighed in its own tank in the liquid state, being transferred from storage tanks where it is also maintained as liquid. This transfer is effected by pulling a vacuum on the weight tank and lifting the sodium up from the storage tanks. The sodium is handled in jacketed pipe or electrically heated pipe and is never exposed to the atmosphere or handled directly by the operator. This insures a tight system which can be adequately blanketed and eliminates, to a large extent, the hazards involved in handling metallic sodium. The beam of the sodium weight tank scale can be so connected that it will stop the flow of sodium when the right weight has entered the weigh tank. The fat and the secondary alcohol required for the reaction may both be weighed in the same tank. As these materials may not have been properly purified before reaching the weigh tank or may have come in contact with water subsequent to purification, it is advisable to provide a safety instrument in this vessel as well, which will detect the presence of water and prevent this material from being fed into the reactor. In all cases it is advisable to keep steam heating and water cooling as remote as possible from this unit, and wherever their use is essential, special thought and consideration should be given to the possibility of steam or water entering the process system. It is important to realize that while very small quantities of water may not necessarily cause a fire or an explosion, very small percentages of moisture reacting with the sodium to form sodium hydroxide will saponify the fat or oil being fed to the unit, forming a soap that will not be reduced or significantly decrease the yield and possibly cause processing trouble because of emulsion formation in subsequent operations. After all of the feed has entered the reactor, the agitator should be run for a short time to make certain that the reaction has become as complete as possible.

The batch is now ready for quenching. If a gravity system is used for dropping the sodium from the weigh tank into the reactor and then dropping the reaction mix from the reactor to the quench tank, it is obviously possible to drop sodium directly from the weigh tank through the reactor and into the quench tank. This must be avoided at all costs. A satisfactory system of interlocked valves can be provided which will prevent the operator from consciously or unconsciously dropping sodium into the quench tank. Prior to the quenching operation, the material of construction used on all equipment may be carbon steel. During the quench operation, sodium hydroxide is formed. If iron free caustic is desired as a by-product from this process, it is then advisable to make the quench tank out of nickel-clad steel. This unit should also be provided with an agitator, a cooling jacket, and a condenser. While there is little heat liberated during the quenching operation because of the conversion of sodium alcolates to fatty alcohols and sodium hydroxide, there is always the possibility that some unreacted sodium will enter the quench tank. The jacket and condenser are necessary for removing the heat of reaction of the unreacted sodium with water. After the entire batch has been dumped into the quench tank, it is only necessary to continue agitation for a few minutes as this reaction goes quickly into completion. The agitator in this vessel should be mild in order to minimize possibility of emulsion formation. The agitation is then stopped, and the liquid is permitted to settle. It is possible to begin with drawing the lower caustic layer almost immediately as there is an appreciable specific gravity difference between the water and oil phases.

A sizeable "look box" should be provided so that the inter-face between the water and oil layers is easily observed. It is then only necessary for the operator to switch valves so that his caustic stream goes to caustic storage while the organic layer is pumped to distillation feed storage. The organic layer is then processed by fractionating the reducing alcohol and inert solvent from the production alcohols. The reducing alcohol and inert solvent are taken as overheads and the crude fatty alcohols as bottoms. The alcohols thus produced may be used as is or may be further distilled or fractionated into component cuts as required.

Sulfonation and Sulfation of Oils

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IT WAS JUST 125 years ago, in 1831, that Fremy discussed the reaction of sulfuric acid and olive oil. In 1870 castor oil was first used in the preparation of a sulfated oil and called "Turkey Red Oil" since for the first time the textile industry was able to obtain a bright red color in the dye bath, a color which had been impossible with the soaps available up to that time. Since then practically every known oil and fat has been sulfated. Twitchell (12) in 1899 mixed oleic acid with members of the aromatic series which, after sulfonation, gave products with much greater resistance to breakdown in solution. Up to about 1930 there were few developments of importance as most efforts were directed to improving the products and aimed at overcoming the presence of the water of reaction. Also numerous studies were being made as to the constituents of sulfated oils and the mechanism of the reactions involved.

Over the years there has been considerable confusion in the literature in regard to sulfonated and sulfated products. It is generally agreed however that a sulfated product is one in which the linkage is carbon to oxygen to sulfur while a true sulfonate is one in which the sulfur is directly linked to the carbon. When this linkage is direct, the resultant product is highly resistant hydrolysis.

In the early '30's considerable work was done in developing methods of fractionation of the sulfated oils. Hart (4) in 1937 proposed a method for the fractionation of sulfated products, and as a result considerable progress has been made in determining the mechanism and the products of reaction.

In 1939 Koppenhoefer (5) and a little later Burton and Robertshaw (1) made the first major attempts to correct the nomenclature and to arrive at the chemical constituents of sulfated oils. The former has evaluated castor, neatsfoot, and cod oils, and his conclusions are in accord with Burton and Robertshaw, who have discussed the subject at greater length. Rueggeberg and Sauls (9) have also discussed some of the reactions, but essentially the reactions as listed by Burton and Robertshaw are generally accepted and listed as follows:

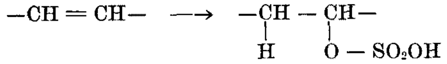
1. Saponification of the glycerides with the formation of free fatty acids. The sulfuric acid acts as a catalyst, but the degree of hydrolysis varies with conditions of the reaction and sulfating may occur before, during, or after hydrolysis. Mono- and diglycerides may be formed as well.

2. Esterification of hydroxyl groups (if present):

$$-CH=CH-CH_2OH + H_2SO_4 \longrightarrow$$
$$-CH=CH-CH_2-O-SO_2-OH + H_2O$$

   The double bonds are not attacked in unsaturated hydroxy compounds until the hydroxyl groups have been removed by esterification or other means.

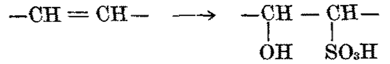
3. Combination with any of the double bonds yielding a sulfuric ester.



$$-CH=CH- \longrightarrow -\underset{\displaystyle H}{\underset{|}{CH}}-\underset{\displaystyle O-SO_2OH}{\underset{|}{CH}}-$$

   These sulfuric esters are unstable and hydrolyze even on long standing into hydroxy-fatty acids and sulfuric acid. This reaction takes place during the sulfation process and the washing process. Since the hydroxy-fatty acids are very reactive under the condensing influence of sulfuric acid, many complicated sulfuric esters may be produced.

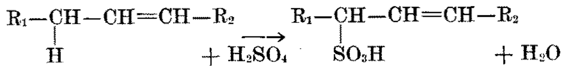
4. Combination with double bonds giving sulfonic acids.



$$-CH=CH- \longrightarrow -\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle SO_3H}{\underset{|}{CH}}-$$

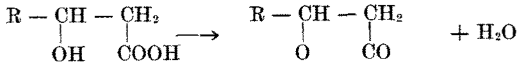
   The sulfonic acids are not completely hydrolyzed by acid or alkali so that the complications described in the preceding paragraph do not take place.

5. Combination at the CH_2 group adjacent to the unsaturated $-CH=CH-$ group.



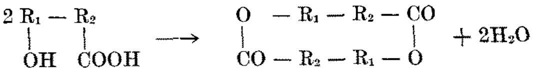
$$R_1-\underset{\displaystyle H}{\underset{|}{CH}}-CH=CH-R_2 + H_2SO_4 \longrightarrow R_1-\underset{\displaystyle SO_3H}{\underset{|}{CH}}-CH=CH-R_2 + H_2O$$

6. Lactone, lactide, and estolide formation.
   The hydroxy-acid may lose a molecule of water giving a lactone, or inner anhydride.



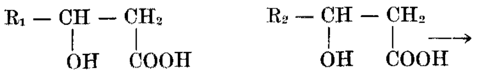
$$R-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle COOH}{\underset{|}{CH_2}} \longrightarrow R-\underset{\displaystyle O}{\underset{|}{CH}}-\underset{\displaystyle CO}{\underset{|}{CH_2}} + H_2O$$

   Two molecules of hydroxy-acid may condense with loss of two molecules of water giving a lactide.

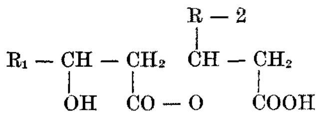


$$2\,\underset{\displaystyle OH}{\underset{|}{R_1}}-\underset{\displaystyle COOH}{\underset{|}{R_2}} \longrightarrow \begin{array}{l} O-R_1-R_2-CO \\ |\qquad\qquad\qquad\ | \\ CO-R_2-R_1-O \end{array} + 2H_2O$$

   The carboxyl group of one acid may react with the hydroxyl group of another acid, giving an estolide.



$$R_1-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle COOH}{\underset{|}{CH_2}} \qquad R_2-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle COOH}{\underset{|}{CH_2}} \longrightarrow$$



$$R_1-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle CO-O}{\underset{|}{CH_2}}\ \overset{\displaystyle R-2}{\overset{|}{CH}}-\underset{\displaystyle COOH}{\underset{|}{CH_2}}$$

One molecule of water from two molecules of hydroxy-acid, or two molecules of water from three molecules of hydroxy-acids, etc., result in complex estolides which saponify with difficulty.

PROCESS CONDITIONS of sufation have varied over the years and are entirely empirical. They entail the gradual addition of an excess of cold concentrated sulfuric acid to the oil, with good agitation and cooling, in a batch operation. After completion of the sulfation the mass is washed, separated, and finished.

In the early days stone crocks of not more than 5-gal. capacity were used. As late as 1942 one manufacturer in Germany used a battery of 50, which when in operation necessitated the addition of the acid six times a day over a period of 48 hrs. After each acid addition the oil was stirred by hand paddle, and after reaction was judged to be complete, was washed several times over another 48-hr. period, which with settling time necessitated a six-day cycle.

However economics demanded larger production, and equipment was devised to handle larger batches. Generally a lead-lined tank with vertical agitator with side arms, operating at slow speeds, was used. In 1920 K. Loffl (6) found that by special agitation the sulfation time could be reduced from five hours to 15 min. While this had no immediate application, it has become of great interest because of the greatly increased production of the sulfonation industry, and today it is possible to have this reaction occur almost instantaneously.

In the sulfation of oils this is not always desirable, and because a lot of oils are sold on customer specification, generally a vessel of a size to permit the treatment of 10 barrels of oil is selected, oftentimes in a battery so that several can be operated simultaneously. This vessel should be lead-lined, of Monel metal or nickel-clad steel, preferably with a jacket and cooling coils. In some instances a turbine type of agitator is selected because of the tremendous differences in viscosities encountered when sulfating various oils and fats.

It is a well known fact that all reactions are controlled by temperature, pressure, concentration of reagents, and catalysts.

In the sulfation process the first and third factors are of the most importance and, of course, are related one to the other. For the most part the lowest temperature possible is the most desirable. As the coolant is to dissipate the heat of reaction, even city water with as high as 75° temperature can be used. Since it requires considerable time for the reaction, there are perhaps undesirable end-products. Ordinarily an ice machine is used so that the oil can be pre-cooled prior to addition of acid and the reaction. Unless the agitation has a scraping action, the cooling jacket by itself is not enough and generally coils are used to effect better heat transfer. Liquid CO_2 has been used, introduced directly into the reaction in liquid form. This allows for much lower temperatures, but if the reaction product has a very high viscosity, the gas cannot readily escape and foaming occurs to a considerable extent.

In regard to concentrations the amounts of the reactants in contact with each other at any given time is of utmost importance and is usually determined by the degree of mixing. Ordinarily the oils are treated with 15 to 33% of their weight with sulfuric acid, and the amount of acid present will certainly have a bearing on the products formed. The acid itself acts as a diluent or solvent, and on normal operations the excess present may run to 85% as sulfuric acid. The progress of the reaction may be judged by an experienced operator by the smell, viscosity, and appearance in solution as well as by the time of reaction.

When the reaction is completed, the next step is the washing operation. This is accomplished by dilution of the mass with water, glauber salt solution, and perhaps the neutralization of the mineral acid. The washing procedure is the most important part of the entire process. From the time that the acid is introduced into the oil, until the oil is actually finished, there is a constant change in the products produced, and the washing operation is conducted at the highest temperatures. In earlier discussion on the mechanism of the reaction, emphasis was on the formation of the esters, but in this operation interest lies in stopping the reaction except for the products desired.

If to castor oil (free from moisture and albuminous matter) 25% of commercial sulfuric acid is added as rapidly as possible, so that the temperature of reaction does not exceed 90°F., and the mixture is agitated for an hour after the acid is all introduced, and then the oil is allowed to lie over night, the next morning the oil should be brilliantly clear in aqueous solution.

The sulfation has gone to completion at this point, and the nature of the finished product will be determined by the subsequent treatment. If the oil is dropped into glauber salt solution, allowed to settle so that the spent acid layer can be drawn off, and then finished with alkali, the resultant product will have a high free fatty acid content, or a high total alkali content according to the amount of alkali added in the finishing. If however the excess acid is neutralized and allowed to settle, so that the salt water can be drawn off, and the oil then finished, the resultant product will be different from the former product in that the free fatty acid and/or total alkali will be lower.

The physical characteristics of the two oils will be different. The quick removal of the excess acid stops or slows down the various reactions even though the temperature is higher. The oil produced will be clear-soluble in a 10% solution, in both very hot and very cold water, and with care will be resistant to acetic acid in solution. The color of the oil will be lighter, and the viscosity, even when cut further with water, will be heavier. The combined SO_3 will also be slightly higher.

Without the quick removal of the acid however, the oil so produced will be darker in color, the solubility in water may be the same, but it will not stand the acetic acid test. Both oils are desirable for certain uses, but the quick acid removal gives a much more uniform product. As can be readily appreciated, there would be numerous variations of these procedures, and in consequence various end-products, even though the actual sulfation were conducted in an identical manner.

WITH OLEIC ACID the procedure is about the same although in this case the reaction moves much more rapidly, so much so that the sulfation and washing are all completed in one day. It is difficult to handle the oil when washing, particularly if one tries to neutralize the excess acid entirely, because of the difficulties of getting a complete separation, and oftentimes the wash is left on the acid side.

Throughout the washing procedure all conditions must remain constant if one is striving for uniformity of product. Temperature control is almost as important in this process as in the actual sulfation. The amounts of wash water, concentrations of alkali or glauber salts, and length of time required for complete removal of the wash water, all have a bearing on the final product. The type of agitation, and the size and shape of the wash tank are also important factors. A wash tank with the capacity equal to three times the volume of the sulfated oil to be processed, with tapered bottom at the draw-off, and equipped with means for mild agitation is recommended. Air can be used, but the least possible amount of mixing is desirable to avoid too complete an emulsification, which in turn would interfere with the separations desired. If necessary to transfer to a finishing tank, this should be done after the acid water is removed.

Oleic acid as well as other fatty acids sulfate in a shorter time than the glycerides. This may be due to the absence of any saponification action, but it would seem that this easier sulfation is more likely on account of the better agitation possible because of the lower viscosity of the acids as compared to the glycerides. This holds true insofar as some of the esters are concerned. Butyl oleate will sulfate at almost the same rate as oleic acid, but in both instances they have a low viscosity.

Sulfated cod oil, on the other hand, presents several problems in its manufacture. Because of its unsaturation the reaction must be rigidly controlled and, for a so-called high sulfation, should be clear in distilled water before washing. It would be desirable to precool the oil before starting the reaction so as to introduce as much acid as possible before the large increase in viscosity takes place and consequent very poor agitation and heat transfer. On account of the heat of neutralization it is oftentimes desirable to give the mixture a quick water wash, and then neutralize the remaining excess acid with careful attention to temperature control.

Tallow, on the other hand, presents a little different problem as it should be run at temperatures just above the melting point. In this instance cooling is difficult as the tallow tends to congeal on the coils, and the thermometer bulb may, or may not, reflect the temperature of the mass. There are compensations however as some types of products require no washing, in which case the entire mass is diluted with water and partially saponified to form a sulfated glyceride soap.

It is well to call attention to the fact that oils which have been washed have also lost some products in the wash water. Most sulfonic acids, if present, will very likely be present in the wash water. There will be small amounts of glycerine when running glycerides and salts from the neutralization of the excess acids. Finally of economic importance there is a loss based on the original oil of at least 4%. This 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,

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

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

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