Sulfated Oils—A Review

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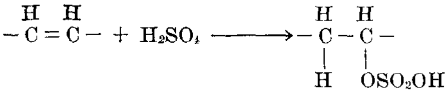
Among surface active agents, there are two that are universally recognized as "old-timers." The origins of the first of these, soap, is lost in antiquity while the second, sulfated oils, is only about 125 years old, having first been reported in the literature by Fremy in 1835 although there is some evidence of their having been experimented with earlier. Between them they have established a pattern of utilization of surfactants which is the basis for a continually expanding industry.

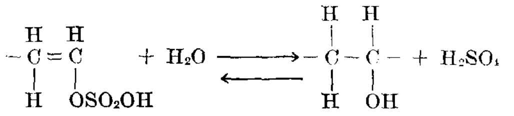
While both have suffered from inroads resulting from the development of modern surfactants, particularly those of petrochemical origin, the impact of these latter materials has been far less on sulfated oils than it has been on soaps. The latest statistical reports on sulfated oils show a continuing production in the U.S. of 40–50 million pounds per year and some private sources feel that captive and other unreported production could easily raise this figure to the 70–80 million pounds per year range.

The commercially important sulfated oils are those prepared from animal fats such as tallow, neatsfoot oil, whale oil, and sperm oil; vegetable oils such as cottonseed, peanut, olive, mustardseed, rapeseed, corn, soybean, and castor; marine oils such as the various fish oils; and fatty acids such as red oil, tall oil, and tall oil fatty acids. These are all classified as nondrying or semidrying oils and cover the iodine value range from about 40 (tallow) to about 140 (fish oils). While higher I.V. oils can be sulfated, polymerization induced by the sulfuric acid usually leads to dark colored, viscous products of limited use. With the exception of castor oil, the reactive grouping in all of these raw materials is the double bond and the sulfation reaction takes place as follows:



$$-\overset{H}{C}=\overset{H}{C}- + H_2SO_4 \longrightarrow -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OSO_2OH}{C}}-$$

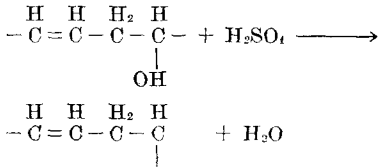
In effect, we have added the sulfuric acid across the double bond and formed the half sulfate ester of a hydroxy acid. As such, this can then be expected to participate in the following equilibrium:



$$-\overset{H}{\underset{H}{C}}=\overset{H}{\underset{OSO_2OH}{C}} + H_2O \rightleftarrows -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}- + H_2SO_4$$

with the water coming from the 96% H_2SO_4 which is used commercially as the sulfating agent. This equilibrium is a limiting factor in determining the extent of sulfation of fatty materials since it has been shown that when the equivalent concentration of the sulfuric acid drops below about 85%, no further increase in combined SO_3 can be expected. In other words, as sulfation proceeds, the effective concentration of the sulfuric acid, in terms of the sulfuric acid and water content of the reaction mixture, drops as sulfuric acid is consumed in the reaction. When this concentration reaches about 85%, sulfation, for all practical purposes, stops. (Schwartz and Perry, Interscience Publishers, 1949, Vol. 1, p. 49.)

In the case of castor oil, a different reaction is involved although the final product is still a sulfuric acid ester. The principal fatty acid in castor is 12 hydroxy, 9-10 oleic acid. The sulfation in this case takes place almost exclusively, under the usual sulfation conditions, at the hydroxyl group:



$$-\overset{H}{C}=\overset{H}{C}-\overset{H_2}{C}-\overset{H}{\underset{OH}{C}}- + H_2SO_4 \longrightarrow$$

$$-\overset{H}{C}=\overset{H}{C}-\overset{H_2}{C}-\overset{H}{\underset{OSO_2OH}{C}} + H_2O$$

In this case, also, an equilibrium is established with the limiting factor again being the equivalent concentration of the residual sulfuric acid.

Some of the older literature indicates that hydrolysis of the triglyceride takes place during the sulfation process with consequent formation of sulfated monoglycerides—the sulfation taking place at the primary hydroxyl of the monoglyceride. Most current workers in this field are agreed that hydrolysis does not take place during sulfation but occurs during the washing procedure which is used to remove the unreacted sulfuric acid.

A typical sulfation procedure is given by Sisley and Wood (Encyclopedia of Surface-Active Agents, Chemical Publishing Company, New York, 1952, p. 51).

"A batch of 30 kg 66°Bé sulfuric acid is slowly run into 100 kg castor oil No. 2. The temperature should not rise above 30°C, which requires the use of cooling coils and the addition of the acid in not less than 2 hours. Agitation is continued for another 2 hours and the mixture is allowed to stand overnight. It is then washed with one and a half times its volume of a 15% solution of sodium sulfate at 50 to 60°C. It is allowed to settle overnight and the acid liquor is drawn off. The washed sulfonate is neutralized and brought to the desired concentration."

While this procedure specifies castor oil, the same basic conditions of time, temperature, and concentrations are applicable to other fatty oils and acids.

The extent of sulfation, i.e. the per cent of SO_3 in the finished oil, is a function of the quantity of acid used. Theoretically, the SO_3 content of a fully sulfated monoethenoid fat as olive oil, or monohydroxy fat, such as hydrogenated castor oil, can be calculated to be in the 20% range. From a practical point of view, it is impossible to attain this SO_3 content from a reaction involving only sulfuric acid and a fat or fatty acid. Values in this range can be obtained by adding a third component to the system such as acetic anhydride or acetyl chloride which act as solvents for the reaction and by reducing the viscosity of the mass permit reaction at lower temperatures while at the same time reacting with and removing the water from the sulfuric acid. Ethylene dichloride or other chlorinated solvents can also be used as the reaction medium and will also yield a higher SO_3 content. In these cases of course, they function as nonreactive solvents which will allow the use of lower sulfation temperatures. The considerable interest in the preparation of high SO_3 oils is evidenced by the many patents covering various techniques to achieve this.

Attempts to achieve a high degree of sulfation almost invariably result in some sulfonation of the oil so that the end product is in part sulfated and in part sulfonated.

At this point, a word about nomenclature in this field is in order. The bulk of the commercial products made by the reaction of unsaturated or hydroxylated fats and fatty acids with sulfuric acid are, as I have indicated, half esters of sulfuric acid. Unfortunately, they are commonly known as sulfonated oils. This gives the connotation, to those familiar with chemistry but unfamiliar with this particular field, of stability to hydrolysis by alkali or acid commonly associated with this structure. As we will see in a moment, sulfated oils do not show this type of stability and are particularly susceptible to acid hydrolysis.

The reaction between the oil and the acid having reached equilibrium, the next problem is to remove the unreacted sulfuric acid and stabilize the sulfated oil. This is done by washing the oil with a salt solution, usually sodium sulfate, with or without the addition of alkali. After thorough mixing, the mixture is allowed to separate and the lower, brine, layer is drawn off and discarded. The remaining oil is then neutralized with alkali and adjusted for water content and titratable alkalinity.

Instead of neutralizing with alkali after washing, it has been found possible to obtain a neutral oil i.e. oil free

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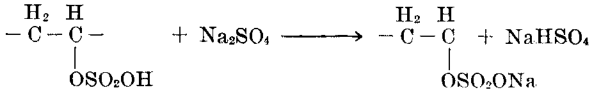
[1] Presented at Northeastern Section, American Oil Chemists' Association, June 6, 1961.

of mineral acidity, by repeated washings with salt solutions. The chemistry involved is:



$$-\overset{H_2}{C}-\underset{OSO_2OH}{\overset{H}{C}}- + Na_2SO_4 \longrightarrow -\overset{H_2}{C}-\underset{OSO_2ONa}{\overset{H}{C}} + NaHSO_4$$

This process has been followed by accurate determination of the sulfuric acid content of the sulfation mass and the subsequent analysis of the wash waters for acidity. The total acidity removed by the washing was shown to be in excess of the unreacted sulfuric acid and by an amount equal to that which would be expected from the amount of combined SO_3 in the oil.

It is during this phase of the procedure that most of the important characteristics of sulfated oils are determined. The oil being washed undergoes hydrolysis (of the triglyceride) in much the same way as in fat splitting with a Twitchell Reagent. At the same time, the sulfate ester is undergoing hydrolysis to the hydroxy acid. This is where the art of the sulfation comes in: in adjusting the conditions of time, temperature, acidity, and salt concentration so that at the completion of the washing period, after the salt layer is drawn off, the sulfated oil will have the properties of solubility, emulsifying power, wetting action, stability, etc. which are desired.

Robertshaw and Burton (Sulfated Oils and Allied Products, A. Harvey, London, 1939, p. 30) show the rate of rise of acid value for a Newfoundland cod oil sulfated with 25% of its weight of sulfuric acid, during the washing period:

Time in wash	A.V.
0	0
3 hours	18.0
6 hours	17.0
9 hours	20.5
12 hours	24.0
15 hours	30.0
18 hours	38.0
21 days	122

Other sulfated triglycerides show a similar pattern of A.V. change. The final A.V. of the oil before neutralization is usually controlled by an empirically determined time-temperature cycle which will vary with the extent of sulfation and acid value desired in the finished oil. An interesting variation of this process, which is particularly useful for obtaining very high acid value oils without endangering the combined SO_3, is covered by U.S. Patent 2,344,154. In this process, the sulfation mass is dropped into a wash which contains enough alkali to neutralize the unreacted sulfuric acid and the combined sulfuric acid and beyond that enough to saponify the oil to the required acid value. After saponification is complete, enough acid is added to split the soap which has been formed and the resulting brine solution is permitted to separate, leaving the oil. By taking advantage of the resistance to saponification of the sulfate ester linkage, as compared to the carboxylic ester linkage in the glyceride, the potential loss of SO_3 in acid hydrolysis is avoided.

The principal variables in sulfated oils, aside from the starting fat or fatty acid are:

a) Organic SO_3 content which is controlled primarily by the amount and strength of the sulfuric acid used in treating the oil and to a lesser extent by the "wash" conditions.

b) The acid value which is controlled by the extent of hydrolysis permitted during the washing phase of the process.

c) The water content of the finished oil, which is usually controlled by the intended use of the product. Most sulfated oils, after washing have a water content in the 20–25% range. Those that are to be used as emulsifiers are usually finished and sold at a water content of 25–30% while those which are to be applied as received or as aqueous solutions or emulsions may be adjusted to water contents of up to 50%.

d) Titratable alkalinity. At least part of the acid value resulting from the hydrolysis in the washing procedure is neutralized with alkali. This improves the water solubility of the finished product and stabilizes it against further hydrolysis.

The pH of sulfated oils is determined by the combination of acid value and alkalinity. In general, the higher the A.V. the lower the pH for the same titratable alkalinity.

With all of these variables, a wide selection of sulfated oils is commercially available with various industries having, over the years, had products developed for them which are specific for their requirements.

The leather industry, for example, makes extensive use of sulfated marine oils in fat liquoring compositions. These are usually medium SO_3 oils (4–6% SO_3) which are applied to the leather (from aqueous emulsions) after the tannage is complete. The oil is absorbed by the leather and provides the internal lubricity which we recognize as softness.

The textile industry makes extensive use of sulfated oils as "textile auxiliaries." Historically, this is the oldest use of these materials, the first application having been as dyeing assistants to permit uniform application of dyestuffs. Sulfated oils are widely used as finishes for textiles and sulfated tallow, for example, is one of the important finishes for cotton fabrics. Here too, it is the softness or low fibre to fibre coefficient of friction which is the desirable characteristic imparted by the use of the sulfated oils.

Sulfated oils are also used in the textile industry as emulsifiers for a wide variety of materials including mineral oil, fatty oils, pine oil, etc. Their use permits the formulation of finishes which will improve the processing of fiber into yarn and yarn into fabric. The emulsifiability of these finishes permits their application from aqueous systems and their removal by simple scouring techniques.

The metal processing industry uses sulfated oil for formulating emulsifiable oils that are used in cutting, rolling, and drawing of various metals. The characteristics of ease of emulsification, emulsion stability, resistance to hard water, and moderate changes in pH which are imparted by the sulfated oils make them the materials of choice for these products.

Shampoos, skin cleaners, and bath preparations based on sulfated castor oil and sulfated vegetable oil are widely used. These are nonfoaming detergents which have an emollient action on the skin and hair and leave them, even after thorough rinsing, with a soft, silky feel.

Many other uses have been developed for sulfated oils ranging from such obvious ones as emulsifiers for various water insoluble materials and wetting and rewetting agents, to less readily predicted uses such as plasticizers for starches, gums, and gelatins, components of defoamers, etc. The essential characteristics responsible for this wide range of application may be summarized as follows:

a) They are surface active fatty materials.

b) Solubility can be varied by relatively minor changes in manufacturing technique.

c) They can be adjusted to blend clearly with and emulsify or solubilize a variety of water insoluble materials.

d) They are resistant to lime soap precipitation.

e) They are stable and active in the pH range of 5.0 to 10.0.

f) They impart the quality of softness to fibrous materials which have been treated with them.

The Bristol Company, Waterbury 20, Conn., announces a line of 4-inch chart width telemeter receivers (Series 670). It also offers a 4-pen Electronic Dynamaster Recorder.

Industrial Instruments, Inc., 89 Commerce Road, Cedar Grove, N.J., offers a solu bridge, designated Model RD-57C, for applications in both plant and laboratory.

The addition of 18 new types of pipets is announced by Kimble Glass Company, a subsidiary of Owens-Illinois, Toledo 1, Ohio.

Induction Heating Corporation, 181 Wythe Avenue, Brooklyn 11, N.Y., has designed and built an autoclave powered by induction heating.