Sulphonated Oils: Their Manufacture, Properties and Uses

Many of the most valuable derivatives of oils and fats are prepared by sulphonation

By H. E. WENNSTRÖM

IN the most strict and well defined sense, "sulphonation" is the term applied to the conversion of organic compounds into sulphonic acids, which is usually effected by the action of sulphuric acid upon the compound which it is desired to convert into a sulphonic acid. The interaction which takes place consists in the reaction between equal molecules of the substance and the sulphuric acid, resulting in the production of a molecule of the sulphonic acid and a molecule of water. The conversion of benzene into benzene-sulphonic-acid by heating with concentrated sulphuric acid may serve as an example of this type of reaction which is represented by the equation:

$$C_6H_6+H_2SO_4=C_6H_5SO_3H+H_2O.$$

Besides sulphuric acid other agents are made use of for effecting direct sulphonation, such as sulphur trioxide, or compounds which readily furnish sulphur trioxide, such as oleum of varying strengths, chlorsulphonic acid, etc.

Direct sulphonation, however, is possible to any large extent only in the case of aromatic compounds, such as hydrocarbons and hydrocarbon derivatives in the benzene, naphthalene, and anthracene series, and in the case of anthraquinone. In cyclic compounds of other types than that of the benzene series it is also possible, as in the case of pyridine, a member of the heterocyclic series, although in this particular instance sulphonation takes place only with difficulty and at a very high temperature.

In the case of compounds not belonging to the aromatic series, such as aliphatic and alicyclic compounds, the conditions under which sulphonation can be brought about are highly variable. On the whole it may be considered as an accepted fact that hydrocarbons in these series are not capable of being sulphonated directly. Sulphonic acids of hydrocarbons of the aliphatic and the alicyclic series are generally obtained either by oxidation of the corresponding mercaptan according to the equation:

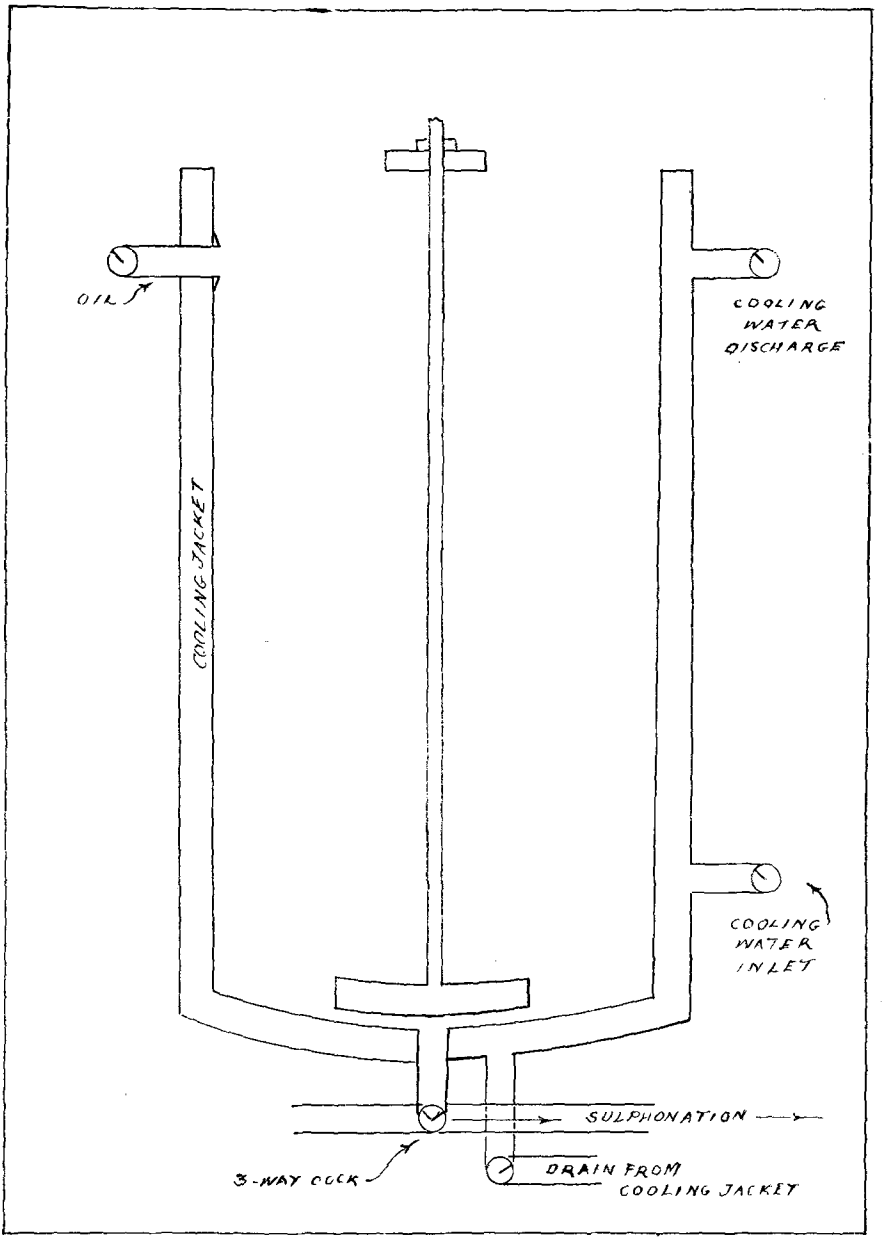
$$2C_2H_5SH+3O_2 \longrightarrow 2C_2H_5SO_3H$$

or by transposition between a halogen derivative of a hydrocarbon and a sulphite, a type of reaction exemplified in the interaction between ethyl bromide and potassium sulphite, resulting in the formation of potassium ethane sulphonate and potassium bromide, according to the equation:

$$C_2H_5Br + K_2SO_3 = C_2H_5SO_3K+KBr$$

It has, however, been possible to bring about direct sulphonation in the aliphatic and alicyclic series in the case of some compounds in these series of a comparatively simple structure, such as for example, acetic acid, which can be converted into sulpho-acetic acid by the action of sulphur trioxide according to the equation:

$$CH_3CO_2H + SO_3 = CH_2{<}\begin{matrix}CO_2H\\SO_3H\end{matrix}$$



Sulphonator—open type

This conversion can be brought about in a different manner, namely by the interaction between sulphuric acid monohydrate and acetic anhydride, according to the equation:

$$(CH_3CO)_2O + H_2SO = CH_2 < \begin{matrix} CO_2H \\ SO_3H \end{matrix} + CH_3CO_2H.$$

Another interesting method of the production of a sulphonic acid in the aliphatic series, is that of methionic acid, which is methane di-sulphonic acid, which results on the absorbtion of acetylene by fuming sulphuric acid followed by treatment of the product with an alkali. Here the process is more complicated, two reactions being involved, in the first instance acetylene unites with sulphur trioxide and sulphuric acid, forming acetaldehyde di-sulphonic acid, according to the equation:

$$C_2H_2 + SO_3 + H_2SO_4 = HCOCH(SO_3H)_2$$

the latter in turn by the action of alkali is split up into formic acid and methane di-sulphonic acid according to the reaction:

$$HCOCH(SO_3Na)_2 + NaOH = CH_2(SO_3Na_2)_2 + HCO_2Na.$$

Another interesting type method of formation of sulphonic acids is to be met with in the alicyclic series or more strictly speaking, in the hydro-aromatic series, and consists in the addition of the elements of sulphur dioxide to a compound containing an ethylenic or unsaturated double bond.

In addition to its use in the proper and strict, well defined sense, as has just been dealt with, the term "sulphonation," has in a loose or general sense been applied to a type of reactions, where there is, strictly speaking, no sulphonation involved, but which are cases of ester formation, the products resulting being for the most part alkyl hydrogen sulphates or acid alkyl sulphates. This latter type of reaction is involved in the production of methyl sulphate (dimethyl sulphate) from methanol and chlorsulphonic acid, and in the preparation of ethyl sulphate (diethyl sulphate) from ethylene and fuming sulphuric acid. This latter process, which is of great technical interest and value, again shows the valuable and important role played by catalysts in this reaction, it having been found that the yield and rapidity of the reaction is greatly augmented by the inclusion of small amounts of certain sulphates, particularly those of copper and silver. Di-ethyl sulphate is a compound of great technical value, serving as an ethylating agent. On account of the large quantities of ethylene produced from petroleum by cracking processes, diethyl sulphate may become of interest as a possible source of a technical supply of ethyl alcohol.

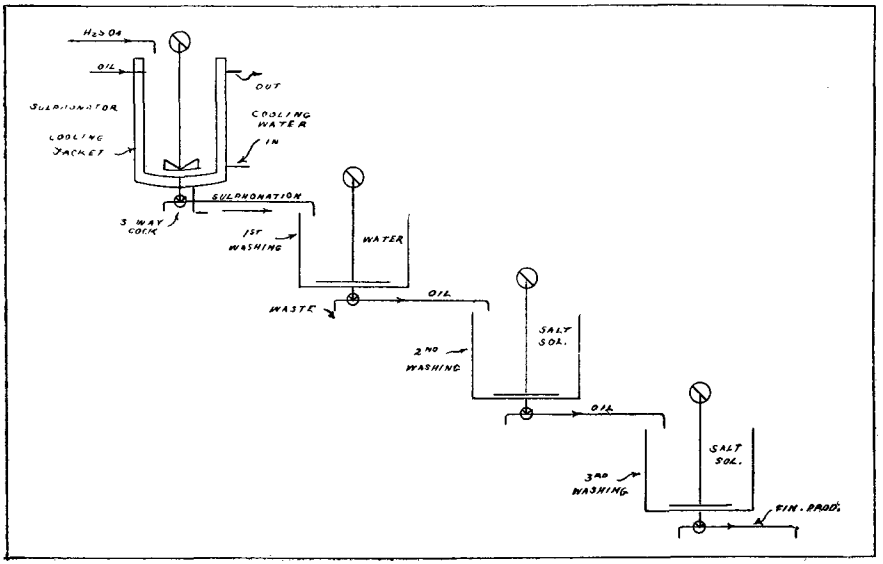
An interesting and technically important field in which processes of sulphonation in either or both of the senses defined above are involved, together with other reactions, is that of so-called sulphonated or soluble oils. We purpose to deal briefly first with the problem of sulphonation of petroleum ois and of petroleum by-products in so far as it is of technical interest.

Sulphonation of Petroleum Oils and Products

While as referred to above it is not possible to sulphonate hydrocarbons of the aliphatic and alicyclic series which make up the bulk of American and Caucasian petroleums respectively, it has, recently, however, been shown, that if the material be first chlorinated, it will then be possible to sulphonate it. This may possibly be accounted for by a loss of resistance to the sulphonating action due to the replacement of hydrogen in an alkyl by another element, in this particular instance by chlorine. The resultant sulphonic acids are of great technical value and interest, seeming to have properties in common

with the corresponding carboxylic acids of a similar number of carbon atoms; thus they form alkali soaps which substantially have all the properties common to soaps. Here, again it may be of interest to note the possible influence of certain catalytic agents known to have a directing influence in the course of sulphonation processes, such as iodine, the tendency of which seems to be an acceleration

Furthermore, it is possible to utilize for sulphonation purposes certain liquid, semi-liquid or solid by-products obtained by the distillation of crude petroleum or shale by a cracking process, such as "paraffine slops," wax tailings, chrysene, or "stillends," or similar material, which may be extracted with gasoline, furnishing a crystalline semi-solid material of either a green or red color. "Paraffine



Sulphonation Layout—Gravity System

of the sulphonation. Thus, it has been shown that in the case of sulphonating benzoic acid, with concentrated sulphuric acid at 175° to 180°C. no sulphonation takes place in the absence of iodine, while in the presence of a small amount of iodine sulphonation takes place quantitatively, the sulpho group entering into the ortho position; whereas in the usual sulphonations with oleum, it enters into the meta and para positions.*

slops" may yield 40 to 45 per cent of this product, and very hard wax tailings, may yield 90 per cent. These products when sulphonated, yield sulpho-acids, which latter, when purified and powdered, are dark green, easily soluble in hot and cold water, and in 50% alcohol, but less readily in strong alcohol. They are but slightly soluble in ether, benzene, or petroleum hydrocarbons. Their neutral salts may be used as detergents, for breaking emulsions, and other purposes, instead of soaps. The alum-

* Ray & Dey, Jour. Chem. Society, 117, 1405. (1920).

inum, lead, and other heavy metal salts are but slightly soluble in water or in dilute alcohol, but are soluble in water or dilute alcohol containing even small amounts of sodium sulphate, carbonate, or chloride.*

Sulphonation of Vegetable and Animal Oils

When certain vegetable or animal oils are treated with concentrated sulphuric acid a chemical change takes place in which several different types of reactions may be assumed as taking place, the exact nature of which it has not been possible to determine so far with any degree of accuracy and certainty. Among oils which are capable of being subjected to this treatment, may be mentioned olive oil, castor oil, cocoanut oil, neats foot oil, and various fish oils. All these oils have been made use of in this type of reaction in the production of preparations for technical purposes.

The general procedure in the sulphonation of oils of the type mentioned is as follows: the oil is treated with an amount of concentrated sulphuric acid amounting to about 20 to 25 per cent of the oil by weight. The oil being contained in a suitable vessel, the acid is added gradually, efficient and continuous stirring being maintained. The temperature is not allowed to rise over 104°F. The color of the ultimate or finished product will be dependent to a large extent upon the color or grade of the oil used at the outset, oils of a pale color and of the first pressing favoring production of light colored products. The nature of the material of the container in which the sulphonation is carried out has been found to have some influence upon the color of the product. It has been found that with lead lined containers products of lighter color have been obtained than in the case where plain wooden tanks have been used. The product of the action of the acid upon the oil is usually allowed to remain 12 to 14 hours after all the acid is in. When the product is completely soluble in a warm alkaline solution, the reaction is finished. The product is washed several times to eliminate the excess of sulphuric acid, at a temperature of 85-95°F., sulphonated oil being insoluble in water containing acid. A quantity of water equivalent to two or three times the volume of the crude mixture is the amount required for washing purposes. The first washing is carried out with pure water, the second with a ten per cent sodium chloride solution, the third with a fifteen per cent sodium chloride solution. The sodium chloride can be replaced by sodium sulphate in the washing. When the product is to be used for certain purposes, the washing is continued until freedom from traces of sulphuric acid is attained (barium chloride test).

Monopole and Tetrapole Oils

Monopole and Tetrapole Oils differ from other products of this class by the fact that their solutions are not rendered turbid in the presence of lime or magnesia.

Monopole Oil: This is a castor oil product, mostly. For its preparation, castor oil or other oil is treated with concentrated sulphuric acid, the resultant sulphonated oils washed and converted into oxy-acids by boiling with water. The oxy-acids are heated to 104-212°F. with a glyceride, and the mixture after cooling is again treated with

* E. M. Johansen. United States Patent 1477829 Dec. 18, 1923.

concentrated sulphuric acid. The resultant product is again washed, and then neutralized according to requirements.

Tetrapole: This is a mixture of carbon tetrachloride with a sulphoricinate soap containing 18 to 27 per cent of fatty acids, and will give a limpid solution, even with hard water.

Uses of Soluble Oils

Soluble oils obtained by neutralization of sulphonated products are employed as mordants, in the dyeing, printing, and dressing of cotton fabrics, in the scouring, softening, milling, and dyeing of woolens, and also, to a small extent in the silk industry. They are also used as tool lubricants in machine shops, being used on machine tools, in drilling, milling, and screw cutting operations.

Oils for Turkey Red and similar processes are produced by the neutralization of the washed sulphonated product with sodium carbonate, sodium hydroxide, or ammonia gas.

Soluble dressing oils such as are used in the tanning industries are usually made by ammonia neutralization, or are a mixture of sodium and ammonium salts.

Sulphonated oils were first used to intensify alizarine dyeings. As wetting agents, and as calcium and magnesium resistant soaps, Turkey red oil and the closely related monopole soap, turkon oil, etc. cannot be replaced by the alkali salts of the fatty acids.

Castor oil soap and other soaps added to the alkaline beta naphthol solution in the production of para red acts in the same way as Turkey red oil, which splits off sulphuric acid on boiling with hydrochloric acid, but not on boiling with dilute sulphuric acid. In its general properties it is similar to soap.

Sulphonation of Fish Oil and of other animal oils: To sulphonate fish oil 3 kilos. of pure sulphuric acid sp. gr. 1.84 are added in portions to 30 kilos of oil saponification number 180 and iodine number 130, in a water jacketed kettle, keeping temperature below 77°F. The product is neutralized by the addition of 5 kilos of concentrated ammonia, keeping the temperature below 75.2°F.* Fish oil sulphonates are difficultly soluble in cold water and thus do not give clear solutions, the solutions have a tendency to solidify to a paste.

P. L. Guilleminot** has carried out a sulphonation of animal oils in the presence of a catalyst, making use of a metal of the iron group, or of an alloy composed of metals of the same. According to example given the process is carried out as follows: iron filings are suspended in fish oil and concentrated sulphuric acid added with stirring. When the reaction is completed, water is added, product is neutralized, if desired, and washed. These sulphonated oils are useful in tanning, dyeing, and soap manufacture.

Blending of Sulphonated Oils

It is possible to combine sulphonated oils with mineral or other unsulphonated oils to form products which emulsify completely with water. Such a combination is covered by a recent patent.*** A water soluble oil is composed of sulphonated castor oil, such as sulphonated Turkey red as a sulphonated fatty or fixed oil, and an unsulphonated oil such as a mineral oil. In an example given, 2

* Heinrich Rose and Maximilian Keh, Collegium, 1924, 327-329.
** Brit. Patent 199743, May 18, 1922.
*** H. W. Hutton, Brit. Patent, 202401, May 18, 1922.

parts of sulphonated fatty oil and an aqeous solution of salt are treated with 6 parts of mineral oil. The mixture is agitated and the acidulated water withdrawn. Two parts of sulphonated Turkey red oil are added and the mixture is agitated and neutralized with a solution of sodium hydroxide in water until slight alkaline reaction, and formation of a complete emulsion with water.

Emulsified Oils

By emulsified oils we understand products somewhat akin to blended sulphonated oils. This type of product is usually derived from olive oil, the lower grades of olive oil containing a large amount (25 to 30 per cent) of free fatty acids, being employed. Or crude grades of olive oil can be subjected to artificial oxidation. It is also possible to use cottonseed oil in combination with free fatty acids; fish oil, and peanut oil as the raw material for making this type of product. When mixed with water, these emulsified oils form emulsions which are more or less stable. They are utilized in the production of the so-called fat liquors used in tanning processes.

Soluble Oil With Mineral Base

By a combination of oleic acid (red oil) with a mineral oil it is possible to produce a so-called soluble oil. This combination is effected by the use of a very small quantity of anhydrous aluminum chloride which exerts a chemical influence making for a change in the nature of the original materials. 60 parts of red oil and 30 parts of mineral oil are mixed, an amount of anhydrous aluminum chloride equivalent to about 1/1000 of the weight of the ingredients is added, and the whole heated to 140°F. when the product becomes black and solidifies. It is saponified with the proper amount of alkaline solution.

Cattle and Sheep Dips

With use of sulphonated oils and blended soluble oils it becomes possible to produce a number of cattle and sheep dips of different types, with or without the incorporation of various ingredients of a disinfecting character.

Ichthyol

Among products obtained by the sulphonation of mineral oils, the ichthyol series of compounds and some of the substitutes for ichthyol are of a special interest, partly on account of their unusual source or derivation, partly on account of their extensive use as pharmaceuticals, mostly for external medication. Most of the compounds of this type are produced by the sulphonation of hydrocarbons containing sulphur, these hydrocarbons may be, either distillates from natural products, such as in the case of the oil serving as a basis for the production of ichthyol, or they may be artificially produced by introduction of sulphur into various sulphur-free hydrocarbons obtained by distillation, such as thiol, tumenol, and thigenol. These basic hydrocarbons or hydrocarbon products containing sulphur are in themselves insoluble in water, but when they are sulphonated, the sulphonic group introduced makes them water soluble and assimilable by the living organism, hence available for therapeutic application.

The entire subject of sulphonation of organic compounds, particularly of oils and fats, offers many opportunities for chemical investigation and technical development.