Sulfonated Oils*

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History

FREMY in 1831 studied the effect of concentrated sulfuric acid on olive oil, oleic acid, and almond oil. The first to prepare a sulfonated olive oil was A. Runge in 1834. He used it as a mordant in dyeing calico red, and thus it may be called the forerunner of the modern Turkey Red Oil. In 1864 Schutzenberger recommended the use of sulfonated oleic acid in aniline black printing (1). In 1875 several colorists prepared sulfonated castor oil products for applying alizarin to cotton. Professor Proctor was probably the first to use Turkey Red Oil in fat-liquoring leather. He did this work in 1890 (1).

Ordinary sulfonated oils are not stable in acid solutions. A great many investigators have tried to overcome this defect either by sulfonating in the presence of a dehydrating agent or by using chlorosulfonic acid or oleum and dehydrating agents such as acetic anhydride (2, 3, 4) or the addition of either chlorinated or other type solvents. The lime soaps of the sulfonated oils are soluble in the chlorinated solvents used.

Originally the name Turkey Red Oil was used to designate sulfonated castor oil. Today it is used rather loosely and may mean any sulfonated vegetable oil. At the present time most of the animal, vegetable, and fish oils as sulfonated oils have been investigated. Today a great many oils are sulfonated either alone or more often as mixtures of oils.

Manufacture

The oil to be sulfonated is placed in tanks containing brine coils for cooling. After it has been cooled to the desired temperature, the acid is added while the oil is being well agitated. It is ideal when all of the acid can be added before the maximum temperature desired has been reached. If this is not possible, the acid is stopped and the oil cooled back 10 to 20° F. and the remainder of the acid added. The acid-oil mixture is generally stirred from two hours to overnight. Most oils are stirred from two to four hours. It is then dropped into a 10° Bé. sodium sulfate or sodium chloride solution, well mixed and allowed to layer. In about an hour the lower layer, containing most of the excess acid and wash water, is drawn off. In practice this is stored and neutralized when making the wash water for the next batch of oil. The heat of neutralization usually heats the wash water sufficiently without the application of external heat. The upper layer or oil layer is then neutralized with alkali nearly to the methyl orange end point. It is left slightly acid to methyl orange. This acidity gives good separation of water with a minimum of decomposition of the sulfonated fraction. The following morning any water that has settled out is drawn off. The oil is then finished to the desired alkalinity and moisture content. The neutralization is usually done with sodium or potassium hydroxide solution. Occasionally ammonia is used.

Some of the older tanners seem to feel that a better piece of leather is obtained by use of an ammonia finished oil. This is open to question. Ammonia finished oils must be kept in a cool place and well stoppered or they will lose ammonia. If sufficient ammonia is lost, the oils will decompose and become insoluble in water. This difficulty is not encountered if the oil is finished with a fixed alkali.

The temperature to which the oil is cooled before adding the acid, depends upon the oil being sulfonated, amount of acid to be added, and the maximum temperature desired. It also depends upon whether or not any true sulfonation is desired along with the usual sulfation. It is usual to cool oils as low as they can be readily stirred, and then adding the acid as rapidly as possible without exceeding the desired maximum temperature. Oils such as neatsfoot, castor, and olive oil do not heat excessively upon treatment with sulfuric acid. Fish oils must be watched more closely for they give off more heat upon sulfonation.

The percentage of acid used depends upon the degree of sulfonation and sulfation desired in the finished product. The percentage of SO_3 in the finished oil is not proportional to the amount of acid used. There is a maximum amount of acid above which no further sulfonation occurs. Most oils are sulfonated with from 17 to 33% of acid based on the weight of oil used. When true sulfonation is desired, it is customary to use at least the same weight of acid as oil.

The strength of the acid used depends upon the degree of sulfonation and sulfation, and body desired in the finished oil. The stronger acids tend to give heavier bodied oils. The acid most commonly used is 66° Bé., which is approximately 93% sulfuric acid. This strength gives a satisfactory product and does not readily freeze during the cold winters. It can therefore be stored in outdoor tanks. Oleum or 98% sulfuric acid when used in weights equal to the weight of the oil tends to form some true sulfonates.

The final temperature depends upon the degree of sulfonation and sulfation, body, and per cent of free fatty acids desired in the finished oil. By free fatty acids is meant those not attached to glycerine or a higher alcohol as in the case of sperm oil. The higher temperatures tend to give heavier bodied oils. This is probably due in part to polymerization, and in part to hydroxy acids. The hydroxy acids are not very water soluble, but they are good emulsifying agents. Hydroxy fatty acids are formed by the hydrolysis of the sulfonated oil, splitting off the sulfuric acid residue and replacing it with an OH group. The higher temperatures also tend to split off glycerine forming more free fatty acids. It also gives a darker colored finished product.

Aging time or time between end of addition of acid and washing depends upon degree of sulfonation and other properties desired. It is usual to continue mixing until two or three drops of the oil-acid mixture in a test tube of water forms a solution. This may be clear, opalescent, or milky, but at least no separation as droplets on the surface of the water occurs.

Wash temperature depends upon oil being sulfonated and per cent free fatty acids desired in the finished oil. If a minimum of splitting off of glycer-

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ine and SO_3 is desired, the temperature of the water is kept low, about 106° F. If more splitting off of glycerine and SO_3 is desired, a higher temperature is employed. About 120° F. is usually sufficient.

Practically any animal, vegetable, or fish oil can be sulfonated, but some only with considerable difficulty. In the case of vegetable oils, the higher the iodine number the more difficult to control the sulfonation. It is usual to blend a non-drying oil with drying or semi-drying oils when they are to be sulfonated with ordinary sulfonating equipment.

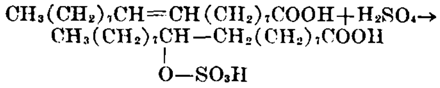
Sulfonated oils are usually sold as 75% or 50% oils. A 75% oil contains about 63% fatty matter, about 25 to 29% water, and the remainder sodium sulfate and impurities.

Properties

Treatment of fatty oils with sulfuric acid renders them water miscible or soluble depending upon the degree of sulfonation. They possess both water and oil soluble groups and hence are emulsifying agents. They are wetting agents, but are not as effective as some of the newer surface active agents. They do possess lubricating properties along with the wetting properties which is sometimes desired. They are acid to neutral and occasionally alkaline in reaction. They are usually finished to a pH of 5.5 to 7.0 using fixed alkalies. If an amine or ammonia is used, a lower pH can be obtained. They do not precipitate with calcium or magnesium salts as readily as soap. The hydroxy acids if formed during sulfonation cause turbidity in the finished product. If present in sufficient amounts, they precipitate out.

The so-called sulfonated oils are really sulfated oils. They are esters instead of true sulfonates. They have the carbon to oxygen to sulfur linkage and not the carbon to sulfur linkage of a true sulfonate. This can easily be proven for, if they be heated with dilute acid for about one hour, all of the SO_3 will be split off rendering the oil insoluble in water. True sulfonates do not generally split off in this manner.

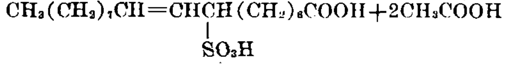
The following equation shows the usual reaction of sulfuric acid on oleic acid:



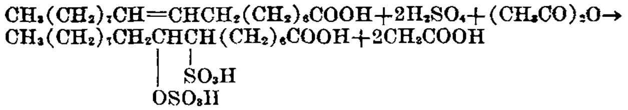
$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + H_2SO_4 \rightarrow CH_3(CH_2)_7\underset{\displaystyle O{-}SO_3H}{\underset{|}{CH}}{-}CH_2(CH_2)_7COOH$$

The sulfuric acid reacts with the double bond to form the ester linkage. The acid residue attaches itself to one of the carbons of the double bond. According to C. Riess (6) if the reaction is carried out at 0° C., the reaction is largely at the double bond to form the ester. If the reaction is carried out around 20° C., considerable splitting of the ester will occur to form hydroxystearic acid and then condensation to form estolides. These are formed when the OH group of one molecule reacts with the COOH group of another molecule.

When true sulfonates are formed, they may be formed by reaction of the sulfonating agent on the hydrogen of a methylene group. According to H. Bertsch (5) the following two reactions occur concurrently:



$$CH_3(CH_2)_7CH{=}CHCH_2(CH_2)_6COOH + H_2SO_4 + (CH_3CO)_2O \rightarrow CH_3(CH_3)_7CH{=}CH\underset{\displaystyle SO_3H}{\underset{|}{C}}H(CH_2)_6COOH + 2CH_3COOH$$



$$CH_3(CH_2)_7CH{=}CHCH_2(CH_2)_6COOH + 2H_2SO_4 + (CH_3CO)_2O \rightarrow CH_3(CH_2)_7CH_2\underset{\displaystyle OSO_3H}{\underset{|}{C}}H\underset{\displaystyle SO_3H}{\underset{|}{C}}H(CH_2)_6COOH + 2CH_3COOH$$

In the case of castor oil, the reaction is practically entirely with the hydroxyl group instead of with the double bond under usual sulfonating conditions. The iodine number of the desulfonated fatty matter is not much lower than the iodine number of the original castor oil. This is not true with the other sulfonated oils where reaction is at the double bond.

Various combinations of products, due to partial hydrolysis of the sulfated portion, may be present in sulfonated oils. Among the possible products are:

- Mono-di-or triglyceride sulfates
- Fatty acid sulfates
- Hydroxy glyceride or fatty acid
  - These can dehydrate to form lactones
  - Two molecules of hydroxy acid can dehydrate to form fatty acid lactides.
- Polymerized products.

The lower temperatures tend to prevent hydrolysis of sulfonated oil to hydroxy fatty acids.

Uses

The oils most commonly sulfonated are castor, cod, neatsfoot, sperm, and various fish oils. Before the war olive and teaseed oils were rather common but today are replaced with other more easily obtainable oils.

In the manufacture of leather the hides are degreased before tanning. After tanning, fatty matter must be replaced in the leather to render it soft and pliable. The leather is drummed in hot water emulsions of the sulfonated oils and raw oils. Sulfonated neatsfoot oil with raw neatsfoot yields a very soft piece of leather. Sulfonated cod oil with raw cod oil yields a drier piece of leather. Sulfonated oils drive the raw oils well into the leather. Soap used as an emulsifier gives more surface lubrication and not as deep penetration into the leather as sulfonated oils.

The paint industry uses sulfonated oils to grind pigments. It has been used in the manufacture of casein paints. The textile industry uses some oils as a lubricant in the spinning and weaving of cloth. In knitting, it is used as a lubricant for the needles and to reduce static electricity. Mixtures of white oil and sulfonated oils having a low free fatty acid content which are easily emulsified in water are required in knitting. Fatty acids are said to attack the needles and hence it is desirable to keep them as low as possible. Some is used in textile finishes, but these are not permanent finishes. They are washed out the first time the garment is laundered. Today they are largely replaced with permanent finishes. Sulfonated oils are used in the dyebaths as wetting agents.

Sulfonated oils are used in a great many industries as an emulsifier for raw oils and paraffine oil. Some is used in the manufacture of so-called non-lathering soapless shampoos. These are composed of sulfonated oil, white oil, and water with sufficient perfume added to give a pleasant odor. Sulfonated teaseed oil or a synthetic oil having approximately the same characteristics is the most desirable oil to use. Sulfonated castor oil has been used in the manufacture of a shampoo, but because of its stickiness it has been largely abandoned in favor of other oils not possessing this stickiness. While this type of shampoo does not form a lather, it does have sufficient cleansing properties to give a clean head of hair after shampooing.

Mixtures containing sulfonated tallow are used as defoamers in the paper industry. In the manufacture of paper, as the wet pulp is brought onto the suction screen or felt, unless something is sprayed on the wet pulp to kill the foam, the paper will be full of small holes called fish eyes. Water emulsions of mixtures containing sulfonated tallow are used for this purpose.

Some cutting oils for the metal working industries use sulfonated oils as emulsifiers for paraffine oil. For this purpose a highly sulfonated sperm oil is probably the most desirable. A good sulfonated sperm oil will easily mix with three parts of paraffine oil to form a clear solution. This will make a stable white emulsion with water.

The cosmetic industry uses some sulfonated oils. Bath oils are often made from sulfonated castor oil, pine oil, or other perfume oils and may contain a water softener. Permanent wave solutions often contain about 1% of sulfonated castor oil.

Large amounts of sulfonated castor oil and derivatives of or from sulfonated castor oil are used in breaking emulsions in crude oil to separate the oil and water fractions.

Castor oil which has been sulfonated and then saponified is used in the textile industry. This is what is commonly called monopole soap.

Sulfonated tallol and mixtures containing tallol are being used as substitutes for sulfonated castor oil. This cannot be used in all replacements, but must be tried out for each replacement to see if it is satisfactory. Sulfonated mixtures containing largely soybean oil are also being used as substitutes for sulfonated castor oil. None of these are replacements for sulfonated castor oil but merely stop-gaps until castor oil again becomes available.

REFERENCES

1. "Sulphated Oils," Burton-Robertshaw, page 1.
2. U. S. Pat. 1,867,954.
3. U. S. Pat. 1,923,608.
4. U. S. Pat. 1,867,954.
5. U. S. Pat. 1,923,608.
6. "Sulphated Oils," Burton-Robertshaw, page 23.

The Effects of Fat Upon the Rates of Digestion in the Human Stomach of Meals of High Protein Content[1,2]

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Introduction

DURING the past decade our laboratory has been engaged in comprehensive experimental studies on human subjects directed to determinations of the influences of fats upon rates of digestion of meals of carbohydrates and proteins in which the fats have been incorporated by physical mixing or cooking. The first report of one phase of these investigations was made to the American Oil Chemists' Society in 1944 (1).

This second report to your Society represents an extension of the earlier studies and the application of different technics, which, however, are directed to the same objectives. The chief difference between the experimental method employed in the studies reported in 1944 and those which will be described in this report is concerned with the evaluation of the time required for complete digestion of a meal in the stomach, which is generally called the gastric evacuation time.

In the earlier experiments gastric evacuations were determined by repeatedly aspirating samples of gastric contents at regular intervals until the stomach was empty (2). This procedure was not utilized in the experiments of two later series included in the present report. In these later experiments the subjects' stomachs were evacuated completely through a stomach tube and the total gastric contents were then analyzed for remnants of the meals.

Experimental Method

The fractional method of gastric analysis (3) was utilized for determinations of gastric secretory responses to the meals.

After the swallowing of the Rehfuss gastric tube the gastric residuum was completely aspirated, and then the meal was fed with the tube in place.

Samples of gastric contents were aspirated at intervals during a period of either two or three hours, or until the stomach had completely evacuated the meal. All of these specimens were analyzed for pH, by means of a glass electrode, free hydrochloric acid (4), total acidity (5), total chlorine (6), and, in one series of experiments, peptic activity (7).

Comparative rates of evacuation of the meals from the subjects' stomachs were determined by aspirating completely the gastric contents at the end of either two or three hours after ingestion of the meals. The instructions given by Hawk and Bergeim were followed in order to assure complete emptying of the stomach (2). Volumes of these specimens were noted and analyses were made of them for total nitrogen (8) and fat (by extraction with ethyl ether).

All experiments were carried out during mornings beginning at 9 a.m. and after a fast for at least 15 hours. On the average, an interval of seven days elapsed between two consecutive experiments on any one subject.

Test Meals

The series of experiments, which are presented in this report, included comparative experimental studies of gastric secretory and motor responses to three

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[2] Presented at the 20th annual fall meeting, American Oil Chemists' Society, Oct. 30-Nov. 1, 1946, in Chicago, Ill.