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PETROLATUM SULFONATE

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This invention relates to the production of sulfonic acids and their salts, especially the calcium sulfonate from hydrocarbon mixtures containing petrolatum.

In the past, sulfonic acids generally have been produced commercially by the reaction of fuming sulfuric acid on liquid hydrocarbons such as mineral oils. For example, they have been obtained as by-products in the manufacture of white oils or medicinal oils, in which process a lubricating oil is treated with fuming sulfuric acid in sufficient quantity to remove substantially all of the coloring matter normally present. According to one conventional procedure employed the sludge resulting from this treatment is allowed to settle and is then drawn off. The treated oil is then washed with water, which is generally discarded, and finally with caustic soda solution. The caustic dissolves the sulfonic acids remaining in the oil and converts them into sodium sulfonates which may be subsequently converted to sulfonates of other metals by familiar methods of metathesis. More recently it has been found that other liquid mineral oil fractions, such as certain petroleum lubricating oil fractions which are not too highly refined, may be sulfonated by methods somewhat analogous to the above with good yields of sulfonated product. Sulfonation of solid hydrocarbons however, such as paraffin wax, by similar treatment with strong sulfuric acid, has given only a trace of sulfonated product.

It has now been discovered that another type of solid hydrocarbon, namely petrolatum, or hydrocarbon mixtures containing petrolatum, may be readily sulfonated to give in many instances the highest yields of hydrocarbon soluble soaps of any naturally occurring petroleum fraction yet tested, yields which may be hundreds or thousands of times greater than those obtained with ordinary crystalline paraffin wax under the same conditions. Furthermore, certain products obtained from the sulfonation of petrolatum or mixtures containing petrolatum are unique in some respects and superior in nearly every respect, particularly for use in compounded oils, to the corresponding products from other stocks.

To illustrate the difference between petrolatum and other fractions from the same crude oil, let us compare the sulfonation of "foots oil" which is one of the preferred forms of the petrolatum of this invention, with similar sulfonation of other fractions from the same crude oil. For example, in the production of an S. A. E. 40 lubricating oil, a residuum from a California crude oil (waxy) may be vacuum distilled to obtain a fraction of

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the desired viscosity. This crude fraction may be first dewaxed by treatment with propane at low temperatures. The dewaxed oil may then be given a moderate treatment with a selective solvent such as phenol, to obtain two fractions, a raffinate fraction of about 80 viscosity index, and the corresponding extract fraction. The slack wax obtained in the above dewaxing step may then be deoiled by treatment with methylethyl ketone at low temperatures to obtain two fractions, one a crystalline paraffin wax and the other a "foots oil" having a melting point of 90° F. to 110° F. Thus, the original vacuum distillate by the above procedure may be separated into the four indicated fractions, all of which have about the same average molecular weight. For brevity these fractions will be termed merely raffinate, extract, wax and petrolatum. Upon evaluating these materials as sulfonation stocks according to (1) yield of sulfonate and (2) quality of the calcium sulfonate concentrate prepared therefrom by the preferred sulfonation process described later, the following data may be obtained:

Table 1

	Vis. index	Pour point, ° F.	Deter- gency, per cent	Anti- corro- sion, hours
Base oil alone S. A. E. 30.....	90	20	60	11
Base oil plus sulfonate concen- trate from—				
Raffinate—yield=3.5%.....	92	20	75	23
Extract—yield=1%.....	65	20	45	7
Wax—yield=.002%.....				
Petrolatum—yield=5%.....	95	0	80	30

In the above tabulation the yield figures are not percentage of each stock sulfonated, but are believed to be proportional thereto, since they are the "CaSO₄ ash" contents of the calcium sulfonate concentrates. These concentrates contain appreciable amounts of unsulfonated hydrocarbons, which are also included in the above blends. Similar effects would be observed also if the unsulfonated hydrocarbons were eliminated, or if a different type of base oil were used in the blends.

In the determination of the CaSO₄ ash, about two to ten grams of the concentrate is weighed into a tared crucible, the crucible and contents are heated and the hydrocarbons are ignited, allowing the combustible material to burn slowly, igniting the residual ash to free it of carbon, adding a few drops of concentrated sulfuric acid to convert any reduced calcium sulfide, etc., to sul-

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fate, re-igniting, and weighing the residue, which is reported as "CaSO₄ ash" in percent of the concentrate tested. It is obvious that this is a reasonably good measure of the degree of sulfonation obtained, and that the petrolatum is an outstanding stock in this respect.

The quality of the calcium sulfonate from the petrolatum is also outstanding, as shown in the tabulated data. In this work, enough of the calcium sulfonate concentrate from each stock is added to the given base oil to obtain a product having a CaSO₄ ash of 0.42%. This product is tested for pour point and for viscosity at 100° F. and 210° F. by familiar A. S. T. M. methods, and the viscosity data are used to calculate the viscosity index as described by Dean and Davis in *Chemical and Metallurgical Engineering*, vol. 36, pp. 618 and 619, 1929. The detergency and anti-corrosion characteristics of the oil are determined by using the base oil containing the sulfonate in a severe service test in an internal combustion (Lauson) engine equipped with copper-lead bearings which are notoriously sensitive to corrosion in this type of service. The bearings are weighed after each 20 hours of service and if the weight loss exceeds about 150 mg. before 60 hours of service has elapsed, they are replaced by Babbitt bearings. The run is discontinued at the end of 60 hours, the engine is dismantled, and the general cleanliness of the inside crown of the piston, inside wall of the piston, the skirt, ring grooves, ring lands, and oil ring slots is noted. The tabulated anti-corrosion figures are interpolated values for the number of hours of operation at the time at which the bearings had lost 100 mg. in weight, while the detergency figures indicate the cleanliness of the engine at the end of the run, 100% being the rating of a perfectly clean engine, and 0% that of the worst possible condition of every one of the above described parts. It is apparent that the petrolatum yields a sulfonate which is outstanding in its effects on viscosity index, detergency, and anti-corrosion, as well as unique in its effect on pour point.

It is an object of this invention to provide a hydrocarbon sulfonation stock and a sulfonation process by means of which sulfonates of special quality, particularly for use in lubricating oils, may be produced.

The sulfonation stock of this invention comprises "petrolatum" by which term is meant to include fractions from petroleum, shale, etc., which contain a sufficient proportion of normally solid hydrocarbons to have melting points above room temperature (above 80° F.) and which do not have a distinctly crystalline structure, but have an unctuous, grease-like texture. Familiar forms of petrolatum in a refined state are the materials known commercially as "Vaseline" and white petroleum jelly. Another form which is to be included in our definition of petrolatum is petroleum foots oil, such as the fraction described above. This generally contains enough semi-solid apparently amorphous material to have a melting point above about 80° F.

It is recognized that the above definition includes two types of material which differ in some properties. For example, "true petrolatum" may be considered as the heavy unctuous material of high molecular weight and high melting point which generally appears in petroleum residue, and is usually present to a much larger extent in Pennsylvania type oils than in California crudes, for example. The foots oil petrolatum

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is a type of "pseudo-petrolatum" of lower molecular weight and lower melting point. (The molecular weight, however, is preferably not less than the average molecular weight of an S. A. E. 30 lubricating oil distillate.) Both of these types of "petrolatum," as defined above, contain normally solid hydrocarbons which differ from the well known varieties of crystalline wax in that they are amorphous or at least micro-crystalline in character, and when sulfonated and neutralized as described later, the resulting calcium sulfonates are obtained in exceptionally high yields, and have the unusual property of pour point depressing action as well as exceptional detergency, anti-corrosion and V. I. improving action.

The process by which the above stocks may be sulfonated may include three steps, namely (1) pre-treatment of the stock, which is described below, (2) the sulfonation proper, which may involve treatment with concentrated sulfuric acid, chlorosulfonic acid, sulfuric acid plus absorbing agents, such as phosphorus pentoxide, etc., and (3) recovery of the sulfonic acids, which may involve neutralization and recovery of the soaps. The preferred method, however, involves suitable pre-treatment of the stock followed by treatment with concentrated sulfuric acid and subsequent neutralization of the reaction product with an excess of the desired neutralizing agent such as caustic soda or lime. This differs from the conventional process utilized in the past in that the more water-soluble "green" sulfonic acids, which in the conventional process dissolve in the acid sludge and the wash water and are not normally recovered therefrom, are converted to soaps which largely remain dissolved in the hydrocarbon phase together with the soaps of the more oil-soluble "mahogany" sulfonic acids. This not only increases the yield of sulfonic acid soaps, but apparently improves the effectiveness of the sulfonates as lubricating oil additives. Furthermore, it is obvious that by elimination of the steps of sludge withdrawal and water washing, not only is there a substantial economy achieved, but the possibility of contamination of the product with iron or lead salts picked up by the action of the acidic materials on the equipment, is avoided. This contamination may be very deleterious especially for sulfonates to be used in lubricating oils.

After adding the excess neutralizing agent, the reaction mixture, plus an oil-soluble diluent if desired, is settled and centrifuged or filtered to remove the solid reaction products insoluble in the oil. If a diluent has been added, it is separated at this point, leaving the soap dissolved in the oil as a sulfonate concentrate. It has been found that when the sulfonation stock contains moderately pre-acid treated petrolatum, the solid insoluble reaction products generally separate with unusual ease.

In order to minimize loss of "green" acids in the water formed in the neutralization reaction or added with the neutralizing agent, the aqueous phase separated in the settling, centrifuging, etc., above may be clarified and part of it recycled with additional neutralizing agent to neutralize additional sulfonated material.

In sulfonating the petrolatum of this invention, it has been found that a certain degree of pretreatment, which we shall designate as "moderate" is desirable. For certain stocks the degree of pretreatment required is critical, as indicated by the following tabulated data. In this work foots oil petrolatum as described above was pre-

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treated at 150° F. to 170° F. with the indicated amount of 95% sulfuric acid in 2, 3 or 4 dumps. The sludge was settled and withdrawn after each dump and the resulting acid oil was then sulfonated and converted to the calcium sulfonate concentrate as described later. The sulfonate "yields" indicated are again the CaSO₄ ash figures for the concentrate. The concentrates were added to the base oil shown to give finished oils of 0.42% CaSO₄ ash, and these were tested in the Lauson engines as in the previous examples. The data obtained follow:

Table 2

	Detergency, per cent	Anti-corro- sion, hours
Base oil alone.....	60	11
Base oil+calcium sulfonate from foots oil petrolatum pretreated with—		
115 lb. H ₂ SO ₄ per bbl. yield=7%.....	55	15
165 lb. H ₂ SO ₄ per bbl. yield=5%.....	80	30
215 lb. H ₂ SO ₄ per bbl. yield=5%.....	80	24
265 lb. H ₂ SO ₄ per bbl. yield=4%.....	70	20

These data show the value of a moderate degree of pretreatment, such as about 125 to 275 pounds of 95% sulfuric acid per barrel and preferably about 150 to 200 pounds per barrel. The degree of pretreatment is not always so critical as the above data indicate, however, when other stocks such as true petrolatum are considered. For example, a crude untreated dark "true" petrolatum obtained from a Utah crude oil may be sulfonated without pretreatment to obtain a product which is approximately comparable in quality to the 115 pound H₂SO₄ pretreated foots oil petrolatum sulfonate of Table 2 and is obtained in about the same yield, the CaSO₄ ash of the concentrate being 7%. Pretreatment which is very severe, however, may reduce this yield of sulfonate somewhat. For example, a true petrolatum from a Mid-Continent crude oil which has been subjected to pretreatment with the equivalent of about 500 pounds of 95% sulfuric acid per barrel of strong sulfuric acid may be sulfonated by the same method to obtain a sulfonate concentrate having a CaSO₄ ash content of only about 3% and approximately comparable in quality with the 215 pound H₂SO₄ pretreated foots oil of Table 2. Pretreatments with 95% sulfuric acid between the limits of about 50 to 500 pounds per barrel result in good quality products, and such treatments may be considered "moderate" for such stocks. The amount and strength of sulfuric acid or other reagent to be used for optimum effects will vary to some extent with the character of the stock to be treated, but in all instances it will be found that the optimum pretreatment is a moderate one, in that more or less pretreatment will tend to give a somewhat inferior product. Conditions of the pretreatment, such as temperature, etc., may be varied as desired as long as the resulting pretreatment is an equivalent one as defined below.

It is to be recognized that the equivalent treatment with selective solvents, such as sulfur dioxide, phenol, furfural, etc., or with polymerizing earths, zinc chloride, aluminum chloride, etc., may be substituted for part or all of the sulfuric acid pretreatment used for any of the above stocks. A convenient means of determining the equivalence of treatments with different reagents is the viscosity index of the treated product. For example, the viscosity index of the foots oil petrolatum of Table 2, untreated, was 63 and after

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treatments with 115, 165, 215, and 265 pounds of 95% sulfuric acid per barrel, this was raised to values of 104, 112, 117, and 119, respectively. It is apparent that for this stock the desired pretreatment with 95% sulfuric acid is one which will raise its viscosity index to about 105 to 120, preferably 110 to 115. Pretreatments of this stock with other strengths of concentrated sulfuric acid or with the other reagents described above, which are carried out so as to yield products of corresponding viscosity index may be considered to be equivalent. Since this type of petrolatum contains an appreciable proportion (about 1/3 to 1/2 in most instances) of normally liquid hydrocarbons, it is also possible to define the range of pretreatment in terms of the viscosity index of a liquid hydrocarbon fraction extracted from the pretreated entire petrolatum. For example, the viscosity index of the liquid fraction of approximately 0° F. pour point obtained by treatment of the above untreated foots oil petrolatum at -10° F. with 5 volumes of an equal volume mixture of methyl ethyl ketone and benzene, filtering the resultant mass, and evaporating the methyl ethyl ketone and benzene from the filtrate, was 28, and the viscosity indexes of the analogous oil fractions from similar treatment of this foots oil petrolatum with 115, 165, 215 and 265 pounds of 95% sulfuric acid per barrel were 54, 66, 80 and 85, respectively. The preferred pretreatment of this stock may therefore be defined as one which will raise the viscosity index of its content of oil of zero pour point to a value between about 60 and 80, and preferably about 65 to 70.

In the sulfonation of the stocks of Table 1, the foots oil petrolatum was pretreated with 165 pounds of 95% H₂SO₄ per barrel as described above. The selective solvent treatment given the dewaxed crude lubricating oil distillate may be considered as a comparable pretreatment of the raffinate of Table 1. The extract and wax fractions were not pretreated. Each stock was then diluted with about 100% of its volume of carbon tetrachloride and treated with about 100 pounds of 30% fuming sulfuric acid per barrel, applying vigorous agitation for 30 minutes while maintaining the temperature between about 120° F. to 130° F. About 200 pounds of lime (97% Ca(OH)₂) per barrel of stock was then added, enough to make the product mixture alkaline, and the temperature was allowed to rise to the boiling point of the carbon tetrachloride, about 170° F., while the mixture was agitated thoroughly. After removal of the solids by settling, decanting, and filtering, the carbon tetrachloride was carefully distilled off to obtain the finished calcium sulfonate concentrate.

In sulfonating the petrolatum of this invention, it is not necessary to use carbon tetrachloride as described above. It is desirable, however, to have the sulfonation stock in a rather fluid form which may be readily and thoroughly contacted with sulfuric acid. For this reason it may be desirable to warm the stock, or to dilute it with an inert material, such as carbon tetrachloride, chloroform, etc., or to sulfonate it in the presence of another more fluid sulfonation stock. The temperature should not be allowed to exceed about 130° F. before the neutralizing agent is added, lest there be excessive decomposition, polymerization, etc., of the hydrocarbons, or excessive corrosion of the equipment. Agitation is generally continued for 10 to 30 minutes after adding the sulfuric acid before adding the neu-

tralizing agent. Shorter times of contact may be used, however, times as short as 0.1 second sufficing where there is sufficiently good contact. After the addition of the excess of neutralizing agent there is less danger of decomposition, etc., and the temperature may be allowed to go higher, but preferably not above about 170° F. The presence of carbon tetrachloride at this stage is of particular value, since allowing it to reflux at atmospheric pressure provides a convenient means of maintaining this temperature as a maximum. Instead of carbon tetrachloride other volatile materials which will reflux at about the same temperature, such as a selected naphtha cut, etc., may be used, especially if added just before or just after the addition of the neutralizing agent. Other diluents of different volatility may also be used, and other means of temperature control employed. Such added diluents perform an additional function in aiding the settling, filtration and/or centrifuging employed to separate the solid products. If soaps other than calcium soaps are desired, neutralizing agents other than lime may be used, with appropriate obvious modifications in technique, or they may be prepared by metathesis of the lime soap in some instances. It is also possible, of course, to prepare the sodium soap by neutralization with caustic soda instead of lime, metathesizing this product to the lime soap thereafter; or to prepare mixed soaps with two or more neutralizing agents.

It has been found that the sulfonate concentrates prepared by the above methods may be treated with a liquefied hydrocarbon gas such as propane at temperatures below atmospheric, to cause rejection of the soaps in relatively pure form from the oil-propane-rich solution. The rejected soaps may then be separated, preferably by settling, and readily freed of residual propane or other volatile solvent by stripping. If desired this liquefied hydrocarbon gas may also be used as the diluent added at about the time of addition of the neutralizing agent, this of course, requiring pressure operation.

No explanation is known for the unique properties of petrolatum as a sulfonation stock. It is known, however, that "petrolatum," as defined above, may include mixtures of oils which are fluid below room temperature with hydrocarbons which are solid at room temperature. For example, the foots oil described above is known to contain both lubricating oil and solid "pseudo-petrolatum" as well as an appreciable proportion of crystalline wax. Such mixtures may in many instances provide superior sulfonation stocks. For example, by separating foots oil into a lubricating oil fraction fluid at room temperature, and a solid fraction of higher melting point than the original foots oil, and separately sulfonating each of these fractions, it may be observed that the calcium sulfonate obtained from neither fraction is as effective as the sulfonate from the entire original fraction, in reducing the pour point of a base oil to which it is added. Similarly, it may be observed in some instances that lubricating oil mixtures containing as little as about 10% of normally solid material having the characteristics of petrolatum exhibit some of the unusual properties of the petrolatum itself as a sulfonation stock. It is part of this invention, therefore, to include in the sulfonation stocks of this invention mixtures of viscous hydrocarbon oils containing at least about 10% of petrolatum. The presence of crystalline wax normally associated

with the petrolatum is also desirable in some instances.

As an example of a process employing sulfonation of mixtures containing petrolatum, the S. A. E. 40 waxy distillate of the original examples above may be given a moderate pretreatment and sulfonated by the preferred methods of this invention, and the sulfonates formed by lime neutralization of the product and the crystalline wax may be separated from the residual oil by propane treatment (the soaps may be preferentially rejected at atmospheric temperature or above and separated, and the wax preferentially rejected subsequently at sub-atmospheric temperature and separated). By such a process the dewaxing is facilitated by the conversion of the amorphous wax to sulfonates; the sulfonates are prepared in high concentration; and an optimum sulfonation stock may be blended.

There is some evidence that an optimum sulfonation stock may be one which contains not only petrolatum, oil and wax, but materials of both high and low molecular weight the "low" molecular weight materials still being in the range of lubricating oils, however.

Modifications apparent to one skilled in the art are to be considered part of the invention as defined in the following claims.

I claim:

1. An improved lubricant which comprises a major proportion of a lubricating oil and a minor proportion sufficient to improve the service characteristics of said lubricating oil of a sulfonate concentrate prepared by contacting a hydrocarbon stock containing at least about 10% of petrolatum with a sulfonation agent, neutralizing the product with an alkaline neutralizing agent, and separating the aqueous phase and the solid oil insoluble reaction products from the resulting sulfonate concentrate.

2. A lubricant according to claim 1 in which the alkaline neutralizing agent is lime.

3. An improved lubricant which comprises a major proportion of a lubricating oil and a minor proportion sufficient to improve the service characteristics of said lubricating oil of a sulfonate concentrate prepared by contacting a hydrocarbon stock containing at least about 10% of petrolatum with concentrated sulfuric acid, neutralizing the entire reaction product with an excess of an alkaline neutralizing agent, and separating the aqueous phase and the oil insoluble reaction products from the resulting oil sulfonate concentrate.

4. A lubricant according to claim 3 in which the hydrocarbon stock is a foots oil petrolatum.

5. A lubricant according to claim 3 in which the alkaline neutralizing agent is lime.

6. A lubricant according to claim 3 in which the petrolatum-containing stock is pretreated prior to its sulfonation, so as to remove therefrom constituents of undesirably low viscosity index, and thereby improve the quality and yield of the sulfonates produced therefrom.

7. An improved lubricant which comprises a major proportion of a lubricating oil and minor proportion sufficient to improve the service characteristics of said lubricating oil of a sulfonate concentrate prepared by contacting a hydrocarbon stock containing at least about 10% of petrolatum with fuming sulfuric acid at a temperature below about 130° F., neutralizing the entire reaction product at a temperature below about 170° F. with an excess of an alkaline neutralizing agent, and separating the aqueous phase and the oil in-

soluble reaction products from the oil sulfonate concentrate.

8. A lubricant according to claim 7 in which the sulfonation is carried out in the presence of an inert diluent.

9. A lubricant according to claim 7 in which the neutralization and separation steps are carried out in the presence of an inert diluent.

10. A lubricant according to claim 7 in which the alkaline neutralizing agent is lime.

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