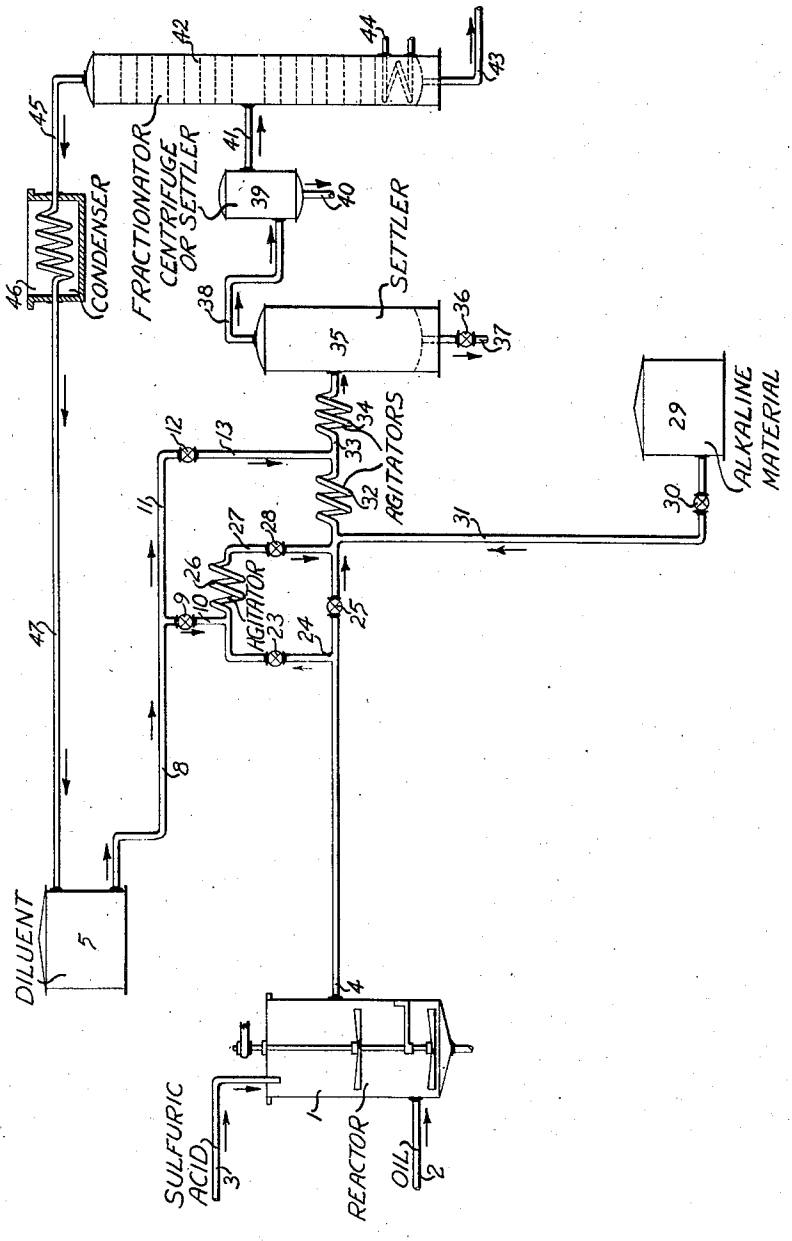
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SULPHONATION PROCESS

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SULPHONATION PROCESS

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This invention relates to the production of sulphonic acids and to the conversion of the sulphonic acids so produced into salts of various metals.

Sulphonic acids are conventionally produced by the reaction of fuming sulphuric acids on various types of mineral oil. One major source for the production of sulphonic acids is from the manufacture of white oils. In the production of white oils a suitable oil fraction, as for example, paraffinic type oil is treated at ordinary temperature with fuming sulphuric acid in sufficient quantity to remove all of the coloring matter present in the mineral oil. As a result of this treatment two types of sulphonic acids are produced. The oil soluble type known as the mahogany acids are left for the most part in the treated oil and the sludge produced during the treatment contains the green acids. Most of the sulphonic acids and the sulphonic acid soaps offered on the market consist mainly of the mahogany acids in the form of their salts.

During the production of sulphonic acid according to present day methods no particular care is taken to prevent contamination of the acids with materials, such as iron and lead, which tends to lower the quality of these acids when used for certain purposes. Usually the treating vessel employed for contacting the mineral oil with the fuming acid is made of metallic lead or steel. Furthermore, after the acid oil containing the mahogany acid is withdrawn from the lead or steel vessel no particular care is taken to prevent contacting this acid oil with transfer lines which are usually composed of these metals. As a result the free acid present in these acid oils dissolves a small amount of the lead and iron which in turn react to produce lead and iron salts of sulphonic acid.

I have discovered a method whereby sulphonic acids may be produced by a process which yields a product in the form of sulphonic acid salt which is substantially free from contaminants. I have also discovered a process whereby sulphonic acids and sulphonic acid soaps can be prepared which contain a major proportion of both the green and mahogany sulphonic acids which distinguishes my product from the sulphonates usually sold on the market which contain for the most part the mahongany acids only.

In preparing the sulphonates according to my invention it is important first to select a lubricating oil fraction which will provide a substantial yield of the desired sulphonate. For this purpose certain lubricating oils of both naphthenic and paraffinic type have been found acceptable and this apparently is true regardless of their viscosity. In general I find that mineral oil fractions which have been prepared by a moderate degree of refinement give the best yield of sulphonic acids. This distinguishes these mineral oil fractions from those which have been highly refined by methods such as severe solvent treatment and from the lightly acid treated mineral oils well known in the art several years ago. In other words, I find it desirable to employ an oil as the base stock for the production of the sulphonic acids which has been moderately treated rather than one which has received little or no treatment or one which has been severely treated. Oils which have been given little or no treatment produce an inferior grade of sulphonic acids because these oils contain fractions which are converted into resinous and sludge-like bodies which contaminate the final product. Oils which have been severely treated usually do not sulphonate very readily and, therefore, oil fractions of this type only produce very small yields of the sulphonated product. To illustrate, a lightly acid refined naphthenic type oil, e. g., Western base oil treated with twenty to thirty pounds of 98% sulphuric acid per barrel is not desirable for the present purpose since practically all of the acid used for the production of sulphonic acid is consumed in producing sludge and the quantity of acceptable sulphonates produced during the sulphonating step is negligible. Similarly, when a highly solvent treated type of lubricating oil, e. g., one of very high viscosity index produced by severe solvent extraction with benzol-sulfur dioxide mixtures, or furfural, or dichlorethyl ether or nitrobenzene is used, the sulphonatable materials of the required type apparently have been largely removed. Any attempt to sulphonate such a severely treated petroleum fraction usually results in the formation of only a small quantity of objectionable sludge.

On the other hand, a naphthenic base oil which has been subjected to a light sulphuric acid treatment (twenty pounds of 98% sulphuric acid per barrel of oil) and also to a moderate treatment with liquid sulphur dioxide so as to yield a lubricating oil of about 25 to 50 viscosity index is an acceptable stock from which satisfactory yields of sulphonates can be produced by treatment with fuming sulphuric acid. Similarly, a mixed base oil moderately treated as by selective solvent extraction to yield a viscosity index of about 80 is an acceptacle sulphonatable stock.

Furthermore, a Pennsylvania oil moderately treated to a viscosity index of 104 and having a viscosity gravity constant of 0.812 is a good sulphonatable stock. However, a medicinal white oil having a viscosity index of 72 and a viscosity gravity constant of 0.826 yields substantially no acceptable sulphonates upon treatment with fuming sulphuric acid. Thus neither viscosity index nor viscosity gravity constant nor, in fact, the type of oil appears to determine what constitutes a good sulphonatable stock. On the other hand, it appears to be the degree of refinement which has here been designated as "intermediate" refinement. Oils of S. A. E. 40 grade have been commonly used but lighter stock such as S. A. E. 20 and heavier stock, such as S. A. E. 60 have been employed.

Specific oils which have been made are given below, the first six being acceptable as satisfactory sulphonatable stock, whereas the last five are of little or no practical value for the production of sulphonates.

Oil type	Treatment	V. I.	V. G. C.	Sulphonate formation
Naphthenic:				
S. A. E. 40	25# H_2SO_4/bbl. followed by SO_2	25	0.862	Highest.
S. A. E. 20	Same as for S. A. E. 40	25	0.862	Do.
Paraffinic S. A. E. 40	Very moderate selective solvent	82	0.815	High.
Pennsylvania S. A. E. 40	Usual (no selective solvent)	104	0.812	Do.
Paraffinic:				
S. A. E. 40	Moderate selective solvent	90	0.804	Good.
S. A. E. 50	Same as for S. A. E. 40	90	0.81	Do.
Paraffinic S. A. E. 40	Heavy selective solvent	100	0.80	Bad.
Paraffin wax deoiled	Normal	130	0.77	Do.
Naphthenic S. A. E. 40	25# H_2SO_4/bbl	−20		Very bad.
Mixed base S. A. E. 10	No treat	−20	0.88	Do.
Medicinal white oil	Heavy	70	0.826	Zero.

In carrying out my process an oil having characteristics like one of the first six contained in the preceding table is rapidly agitated with concentrated sulphuric acid. By the term "concentrated sulphuric acid" I mean sulphuric acid which is of a strength lying between 100% sulphuric acid and pure sulphur trioxide. For practical purposes I find that it is desirable to employ 40% fuming sulphuric acid since this gives the best yield of sulphonic acids.

After thorough agitation of the acid and the oil for a period between about ten minutes and sixty minutes the sulphonated product is withdrawn from the agitator and is contacted immediately with a suitable alkali, such as for example, calcium oxide, or a calcium hydroxide-water mixture, in an amount in excess of that required to neutralize all of the free sulphonic acids and free sulphuric acid present in the mixture. The neutralized mass is then allowed to settle for the separation of the excess alkali and the calcium sulphate which is formed by the reaction of the calcium oxide with the free sulphuric acid present. This separation step may be facilitated by diluting the mixture either before or after the addition of the alkali with petroleum naphtha, liquid propane, liquid butane, liquid pentane or benzol. Furthermore, providing that the solid materials cannot be effectively separated by simple separating means the neutralized mixture may be centrifuged or filtered as a final method of separating any solid matter present in the neutralized mass.

During the neutralization step heat is liberated and if care is not exercised the product will rise to a temperature sufficiently high to cause a proportion of the sulphonic acids present in the mixture to be decomposed. In order to prevent this decomposition it is often necessary to supply some means of cooling the mixture undergoing neutralization to keep the temperature below this decomposition point. As a general rule I find that at no time should the temperature during this neutralization step exceed substantially 175° F.

My process may be more thoroughly understood by referring to the drawing.

Referring to the drawing, the oil to be sulphonated is introduced into reactor 1 through line 2. Simultaneously fuming sulphuric acid is introduced into reactor 1 via line 3. The sulphuric acid and oil in reactor 1 are vigorously agitated and after completion of the sulphonation reaction the sulphonated product is removed from reactor 1 via line 4. The temperature employed in the reactor during the sulphonation reaction is ordinarily maintained at about 135° F., however, the temperature which may be employed in reactor 1 may be varied somewhat and in many cases it may be carried out throughout the range of temperature between 100° F. and 150° F. Likewise the time of contact between the acid and the oil in reactor 1 may vary considerably. For example, I have found that good sulphonated material can be produced by restricting the reaction time to a period of ten mintues or by continuing this reaction time for a period of around sixty minutes. In other words, I wish it to be understood that the contact time between the acid and the oil in reactor 1 may vary considerably and that I may employ a reaction period of from ten minutes to sixty minutes.

The strength of the acid employed in reactor 1 may also vary over a wide range. For example, I have found that 100% sulphuric acid produces a satisfactory product and I have also found that pure sulphur trioxide may be employed. As a matter of practice, however, I prefer to use 40% fuming sulphuric acid since this material is easy to handle in the process and produces a very satisfactory product.

In carrying out the reaction in reactor 1 I have found that when I employ 40% fuming sulphuric acid that it is desirable to use an amount of acid in the reactor which will be equivalent to about 30% of the weight of the oil.

The sulphonated product withdrawn from reactor 1 through lines 4 and 24 and valve 23 is mixed with a diluent withdrawn from tank 5 via valve 9 and lines 8 and 10. This mixture of diluent and sulphonated product passes through agitator 26 where it is thoroughly mixed. The diluents which I may employ include such materials as petroleum naphtha and other light low boiling hydrocarbons, such as liquid pentane, butane, propane or mixtures thereof, or aromatic hydrocarbons such as benzol, toluol or xylene.

After thorough mixing of the diluent and sulphonated product in mixer 26 and withdrawal through line 27 and valve 28, alkali withdrawn

from tank 29 through valve 30 and line 31 is mixed with the diluent and sulphonated product in agitator 32. It is important that the temperature during this neutralization does not exceed 170° F. since above that temperature it will be found that a portion of the sulphonated product will tend to decompose. Various means may be employed to maintain a relatively low temperature of the material in 32. One means is simply to surround the agitator with a liquid cooling medium, such as cold water or brine. Another means which could be employed would be to permit the heat of reaction between the sulphonated product and the alkali to vaporize a portion of the low boiling hydrocarbon diluent into a condenser, not shown, where the hydrocarbon would be liquefied and refluxed back into the mixture.

The specific alkali material withdrawn from container 29 for the above neutralization depends upon what product is to be obtained by the process. For example, if it is desired to produce the calcium salt of sulphonic acids there is withdrawn from container 29 ordinary calcium oxide in a quantity in excess of that which would be chemically required to neutralize the acids present in the mixture flowing into agitator 32. After thorough agitation of the alkaline material and diluted reaction mixture in agitator 32, the mixture then flows into settler 35 via line 33 and agitator 34. In settler 35 the excess alkaline material and sulphuric acid salts in aqueous solution settles out and is withdrawn from settler 35 via valve 36 and line 37. From the top of settler 35 the fully neutralized sulphonic acids in the form of sulphonates in diluted oil solution are withdrawn via line 38 and passed to 39, which may be either a centrifuge or a filter for the separation of any remaining solid alkaline material which has failed to settle out in settler 35. The solid material removed by the centrifuge or filter is discarded through line 40 and the clear diluted solution of sulphonates pass via line 41 into fractionator 42. Fractionator 42 is equipped with a coil 44 for the purpose of introducing sufficient heat into the diluted sulphonate solution to vaporize the diluent present which is removed via line 45 to condenser 46 where the diluent is liquefied and then passes via line 47 back to the diluent storage tank 5. From the bottom of fractionator 42 the sulphonate solution is withdrawn via line 43.

This process can be adapted for the production of a wide variety of sulphonates. For example, I may produce alkaline earth sulphonates by the use of calcium oxide, barium oxide, strontium oxide, or magnesium oxide, or I may produce alkali metal sulphonates by the use of sodium hydroxide, potassium hydroxide or lithium oxide. Obviously any other metallic sulphonate may be produced by the process which I have just described. For example, zinc, aluminum, cadmium, chromium, antimony, arsenic or tin.

In the foregoing description I have described the use of a diluent which is added to the sulphonated product withdrawn from reactor 1 from tank 5, valve 9 and lines 8 and 10. The amount of diluent which I employ at this point may vary. In many instances I find that a one to one ratio of diluent to sulphonated product is sufficient to obtain the desired degree of settling in settler 35. However, in cases where it is desired to increase the rate of settling and the degree of settling it may be found necessary to increase the quantity of diluent employed. For example, in some cases I find that it is desirable to use anywhere from two to five volumes of diluent to one volume of sulphonated product in order to obtain the desired degree of settling in settler 35.

In some cases it has been found that it is more desirable to add the diluent to the sulphonated material subsequent to the addition of the alkaline material to the sulphonated product in agitator 32. This is accomplished by closing valves 23 and 9 and opening valve 25. By this arrangement the sulphonated material in line 4 passes via valve 25 into agitator 32 where it is converted into the sulphonate salt by admixture with the alkaline material withdrawn from container 29, after which the completely neutralized sulphonic acids which are now in the form of salts are diluted with diluent from tank 5 which passes via lines 8 and 13 into line 33 and agitator 34 where the diluent and sulphonate salts containing the excess of alkaline material are thoroughly agitated. In either case the alkalinized material passes into settler 35 where the excess alkaline material is withdrawn, as explained above, through valve 36 and line 37. In many instances it is immaterial whether the diluent is introduced either before or after the sulphonated product is contacted with the alkaline material in agitator 32. However, I have found in some cases that the degree of settling in settler 35 is greatly influenced by the point of introduction of the diluent.

By producing salts of sulphonic acid by the above method I am able to reduce the contaminants which are normally found in the ordinary commercial varieties of sulphonic acid salts now being offered on the market. The methods which I have described for the production of sulphonic acids reduces the tendency of the acidic material withdrawn from reactor 1 from being contaminated with materials which would normally be dissolved by this material. In other words, the product which is withdrawn from reactor 1 contains a substantial quantity of free acid which normally attacks the walls of reactor 1 as well as the transfer lines and results in contamination of the product. However, if the material withdrawn from reactor 1 through line 4 is immediately neutralized for the removal of any free acid from the sphere of activity it is obvious that a product will be obtained which is less contaminated with impurities, such as iron sulphonates, than would be obtained provided this neutralization step were eliminated. In carrying out the process it is essential that the sulphonated product withdrawn from reactor 1 be passed without substantial delay to the neutralization step in 32 in order to prevent the possibility of contamination.

I claim:

1. A process for the production of oil soluble mixtures containing substantial amounts of metal salts of both mahogany sulphonic acids and green sulphonic acids dissolved in lubricating oil which comprises contacting a mineral lubricating oil with concentrated sulphuric acid at a temperature between about 100° F. and 150° F. so as to convert a portion of the said oil to a mixture comprising both oil soluble mahogany sulphonic acids and oil insoluble green sulphonic acids, and immediately thereafter treating the entire reaction product with an alkaline compound of the desired metal in a quantity in excess of that required to neutralize all of the free acids therein, thereby forming a solution of the metal salts

of both the mahogany acids and the green acids in the unreacted oil.

2. A process according to claim 1 in which the solution of metal sulphonates is settled to separate therefrom undissolved inorganic compounds.

3. A process for the production of oil soluble mixtures containing substantial amounts of metal salts of both mahogany sulphonic acids and green sulphonic acids dissolved in lubricating oil which comprises treating a mineral lubricating oil with concentrated sulphuric acid at a temperature between about 100° F. and 150° F. and thereby forming a mixture of sludge containing green acids and unreacted oil containing mahogany acids, and immediately neutralizing said green and mahogany acids with an alkaline compound of the desired metal without separation of sludge thereby causing the metal sulphonates of both the green and mahogany acids to dissolve in the unreacted oil.

4. A process according to claim 3 in which a low boiling hydrocarbon diluent is added to the reaction product before the addition of the alkaline compound.

5. A process according to claim 3 in which a low boiling hydrocarbon diluent is added to the solution of the metal sulphonates and the thus diluted solution is settled for the separation of undissolved inorganic compounds.

6. A process according to claim 3 in which the temperature is maintained below about 170° F. during the addition of the alkaline compound.

7. A process for the production of lubricating oil solutions containing substantial amounts of alkaline earth metal salts of both mahogany sulphonic acids and green sulphonic acids which comprises contacting a lubricating oil of an intermediate degree of refinement with sulphuric acid having concentration greater than 100% at a temperature between about 100° F. and 150° F., thereby converting a portion of said oil to a mixture containing oil soluble mahogany sulphonic acids, oil insoluble green sulphonic acids and unreacted oil; neutralizing the free acidity of the entire reaction product by the addition thereto of an excess of alkaline compound of an alkaline earth metal, thereby converting both the mahogany acids and the green acids to their alkaline earth metal sulphonates and dissolving these sulphonates in the unreacted oil; adding a low boiling hydrocarbon diluent to the said lubricating oil solution of metal sulphonates; and settling the thus diluted solution for separation of undissolved inorganic compounds.

8. A process according to claim 7 in which the alkaline earth metal is calcium.

9. A process according to claim 1 in which the stock is a naphthenic lubricating oil of intermediate refinement.

10. A process according to claim 1 in which the amount of concentrated sulphuric acid employed is smaller than the amount of oil treated, and the temperature during the sulphonation is maintained below about 150° F.

11. A process according to claim 7 in which the temperature is maintained below about 170° F. during the neutralization by evaporation of diluent.

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