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PROCESS FOR FRACTIONATION OF SULPHONIC COMPOUNDS

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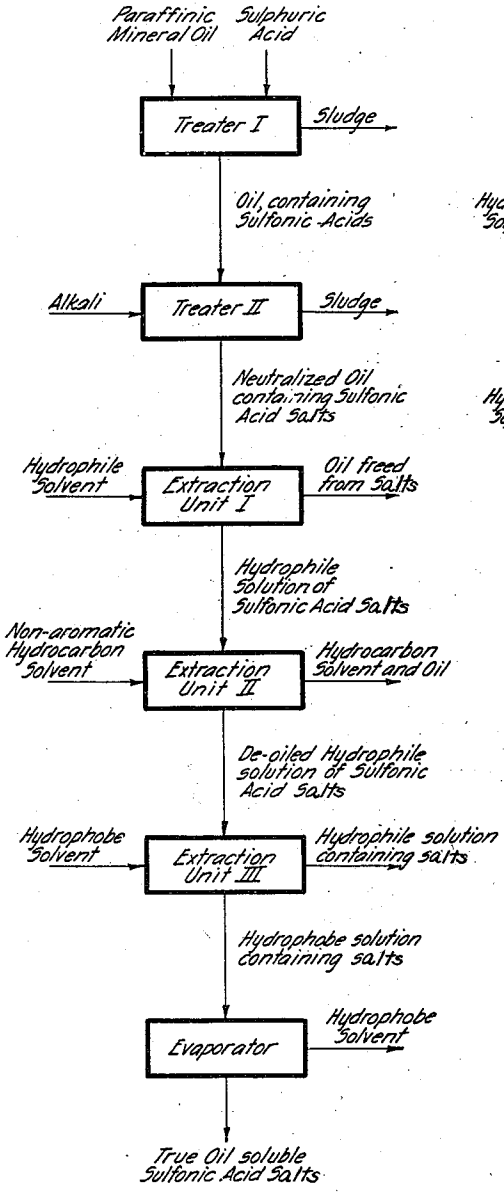

Fig. 1.

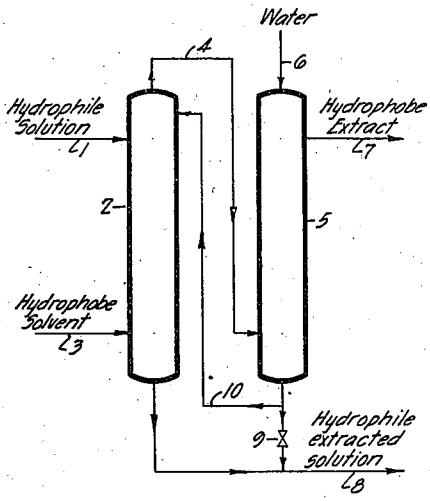

Fig. 2.

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PROCESS FOR FRACTIONATION OF SULPHONIC COMPOUNDS

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8 Claims. (Cl. 260—504)

This invention relates to the fractionation of sulphonic compounds, particularly of the type produced in treating paraffinic mineral oils with strong sulphuric acid. The term "sulphonic compounds" as herein used refers to free sulphonic acids and/or salts thereof. Alkali salts of sulphonic acids are widely used as detergents, emulsifiers, wetting agents, binders, substitutes for asphalts, fireproofers, etc.

It is known that when mineral oils are treated with strong sulphuric acid several types of sulphonic acids may be produced. One type which is readily soluble in hydrocarbon oils as well as in many aqueous organic solvents is known as mahogany acids. Another type which is less readily soluble or insoluble in hydrocarbon oils but soluble in water and aqueous organic solvents is known as green acids. Certain green acids, although insoluble in hydrocarbon oils, became at least partly soluble in hydrocarbon oils in the presence of mahogany acids.

The alkali salts of these acids have solvent properties quite similar to those of the free acids. Because of their solubility both in hydrocarbons and aqueous solvents, mahogany salts are especially valuable as detergents and emulsifiers.

Inasmuch as different types of sulphonic compounds have widely different properties and uses, it is highly desirable to separate them from each other as fully as possible. It is an object of this invention to provide a process for separating mixtures of different types of sulphonic compounds, which by virtue of the mutual solutizing influence of their components are completely soluble in hydrocarbon oils, only a fraction of which, however, is soluble therein when separated, the other fraction being substantially insoluble in hydrocarbon oils. It is a further object to produce in a simple manner substantially pure true oil soluble sulphonic compounds which consist essentially of a single type and which are substantially free of sulphonic compounds difficultly soluble in oil.

I have discovered that hydrocarbons consisting of a simple aromatic nucleus to which is attached at least one long aliphatic side chain, for instance, as cetyl benzene or cetyl xylene, yield upon sulphonation sulphonic acids which are more easily soluble in hydrocarbon oils, particularly aromatic hydrocarbon solvents, and their salts exhibit better detergent and emulsifying properties than sulphonic acids and salts respectively produced from hydrocarbons of about the same number of carbon atoms comprising a more complicated aromatic nucleus of the type of naphthalene, diphenyl, anthracene, chrysene, etc. with at least one long side chain or a simple nucleus with many short side chains such as dioctyl benzene or trihexyl benzene.

Depending upon the nature of mineral oils treated and the strength of the sulphuric acid used, varying quantities of mahogany and green acids are produced. Relatively high yields of mahogany acids are obtainable from paraffinic oils boiling above kerosene and containing the desired type of sulphonatable hydrocarbons, such as Pennsylvania wax distillates and lubricating oils, or raffinates produced in the solvent extraction of mixed base relatively high boiling oils, while so-called naphthenic oils such as Gulf Coastal and similar oils, extracts of mixed base oils, or relatively low boiling oils, in general, yield largely green acids.

In order to produce sulphonic acid salts of the highest detergent and emulsifying qualities I have invented two lines of approach. I may synthetically produce the desired hydrocarbons, for instance by reacting chlorinated paraffin wax with benzene or a homologue thereof in the presence of a Friedel-Crafft catalyst such as aluminum chloride, zinc chloride, boron fluoride, ferric chloride, phosphorus pentoxide, etc. under conditions to produce benzene derivatives having at least one paraffin-like hydrocarbon attached as a side chain; or by cracking in the vapor phase or preferably dehydrogenating paraffin wax and fractionally distilling the resulting product under conditions to produce long chain olefines of 10 or more carbon atoms, and condensing same with benzene in the presence of a suitable condensation catalyst such as phosphoric acid, sulphuric acid, phosphorus pentoxide, etc. to form similar long chain alkylated benzene derivatives. The products of alkylation are then sulphonated to produce sulphonic acids, and the acids or their salts are separated from impurities and unreacted hydrocarbons by known methods.

The other line of approach with which this invention is particularly concerned, comprises sulphonating a suitable paraffinic mineral oil of the type afore described and separating the resulting sulphonic acids or their salts from unreacted sulphuric acid, mineral oil, and sludge by known methods. Due to the solutizing effect which the truly oil soluble sulphonic compound exert on less oil soluble sulphonic compounds the oil phase after separation contains, together with oil soluble sulphonic compounds, a considerable quantity of sulphonic compounds which, by themselves, are substantially insoluble in the oil. Sul-

phonic compounds isolated from the oil phase are thus mixtures containing varying quantities of water-soluble sulphonic acids or salts which are difficultly soluble in hydrocarbon oils. In my process I separate mixtures of truly oil soluble and difficulty oil soluble sulphonic compounds by extracting such mixtures either in the acid, neutral or alkaline state simultaneously with two organic solvents which are substantially immiscible with each other, one being hydrophobe and the other being hydrophile, under conditions to effect a distribution of the compounds in the two solvents, separating the solutions so obtained from each other and separating the solvents from the acids or salts in any suitable manner such as by salting out, or preferably by distillation. To increase the immiscibility of the hydrophobe and hydrophile solvents, and to raise their relative solvent powers and selectivity for the two types of sulphonic compounds, I usually add a substantial amount of water to the hydrophile solvent.

If desired, the mixture of compounds may be first dissolved in one solvent, and the solution so obtained may then be extracted with the other solvent under conditions to effect a separation. My preferred procedure consists of dissolving the mixture first in the hydrophile solvent and extracting the resulting solution with the hydrophobe solvent. In this last manner separation of mahogany and green acids or salts thereof is most easily achieved, since both types of compounds are soluble independently of each other in the hydrophile solvent, but only the true mahogany compounds are readily and independently soluble in the hydrophobe solvent.

Salts separated from the extract contained in the hydrophobe solvent possess the desired high detergent and emulsifying properties.

Suitable hydrophobe solvents are aromatic low boiling hydrocarbons as benzene, toluene, xylenes, ethyl benzene, etc. although aliphatic and naphthenic hydrocarbons as naphtha, petroleum ether, cracked and straight-run gasoline distillates, gasoline extracts, etc. may also be used. Halogenated hydrocarbons such as carbon tetrachloride, di-fluor di-chlor methane, chloroform, ethyl chloride, di-chlor ethylene, tri-chlor ethylene, propyl chloride, di-chlor propane, etc. are suitable as well. Aromatic hydrocarbons and in particular toluene, or mixtures of hydrocarbons containing high percentages of aromatic hydrocarbons are preferred because they appear to have the greatest solvent power for the desired sulphonic acids or salts.

The hydrophile solvent which is used to dissolve or keep in solution the less desirable sulphonic acids or soaps may be selected from the group of oxy- and/or amino hydrocarbons or substituents thereof, which at ordinary room temperatures are miscible with water preferably in all propertions and which at least in the presence of water are substantially immiscible with hydrophobe solvents. This group comprises the lower mono-hydric alcohols of less than 4 carbon atoms; poly-hydric alcohols as ethylene glycol, glycerine; lower ketones as acetone, methyl ethyl ketone; acetals, ethylene glycol mono-alkyl ethers, di-ethylene glycol alkyl ethers, halogenated lower alcohols, etc.; ethylene diamine, amino ethyl alcohol, etc.; also carboxylic acids such as formic, acetic, propionic, butyric acids, etc. may be used if the extraction is carried out on mixtures of the free sulphonic acids rather than of their salts; selective solvents of the type used in the fractionation of hydrocarbon oils such as liquid SO_2, furfural, $\beta\beta'$ di-chlor ethyl-ether, phenol, cresilic acids, nitro benzene, acrilic aldehyde, croton aldehyde, etc. may have a limited application if used in combination with a hydrophobe solvent which is only partially miscible or preferably substantially immiscible therewith.

The attached drawing shows flow diagrams of my process; Figure 1 presents diagrammatically a series of treating steps which may be employed in my process, while in Figure 2 a method of extraction is shown which is applicable in connection with the treating procedure as shown in Figure 1.

Referring to Figure 1, suitable mineral oil heavier than kerosene is treated with strong sulphuric acid which may or may not be fuming, in treater I according to established procedures such as are, for instance, practiced in the manufacture of medicinal oils, paraffinum liquidum, transformer oils, etc. The acid may be added in one or several dumps, and sludges may be withdrawn after each dump by settling, centrifuging, or precipitating with a finely divided solid as clay, diatomaceous earth, etc.

The substantially sludge-free but acid-reacting oil containing oil soluble sulphonic acids and a small amount of entrained unreacted sulphuric acid is neutralized in treater II preferably with an alkali metal hydroxide, although ammonia or alkali earth and other metal hydroxides may often be used instead. If sludge is formed, same may be withdrawn. The neutralized oil is now extracted in an extraction unit I with an aqueous organic hydrophile solvent of the group hereinbefore described. The most commonly applied solvents are 50% aqueous ethyl alcohol or 85% aqueous ethylene glycol. The extraction is carried out under conditions to effect a substantially complete transfer of the sulphonic acid salts from the oil to the hydrophile solvents. This can easily be achieved in a multi-stage countercurrent extraction system. The resulting mineral oil, free from sulphonic acid soaps, is withdrawn, and the hydrophile solution containing sulphonates and small quantities of sulphate and mineral oil is extracted in extraction II with a relatively small amount of a non-aromatic hydrocarbon solvent such as naphtha, preferably straight run from a paraffinic crude, butane, pentane, hexane, cyclohexane, etc. under conditions to dissolve the mineral oil and to leave the salts substantially completely in the hydrophile solution. To accomplish this it is desirable that the ratio of hydrocarbon to hydrophile solvents be below about 1:2, and the extraction is preferably not carried out in countercurrent. Ordinary batch washing at temperatures not substantially above ordinary room temperature is usually quite suitable. If desirable, the concentration of salts in the hydrophile solvent prior to extraction in unit I may be increase by evaporating at least a portion of the hydrophile solvent.

The de-oiled hydrophile solution is now further extracted in an extraction unit III with a hydrophobe solvent of the type described, under conditions to transfer a substantial portion of the sulphonates contained in the hydrophile solution to the hydrophobe solvent. This may be achieved by counterflowing the two solvents, if desired in several stages. In Figure 2 an illustrative diagram of a suitable extraction process is shown in which the de-oiled hydrophile solution enters through line 1, into an extraction tower 2 near its top, while the hydrophobe solvent, such as toluene, enters through line 3 into the lower part

of tower 2. The hydrophobe solvent rises to the top, dissolving at least a portion of the preferred truly oil soluble sulphonates together with a relatively small portion of hydrophile solvent and a trace of difficultly oil soluble sulphonates. This extract is transferred through line 4 to extraction tower 5 in which it is washed with water from line 6 to remove dissolved hydrophile solvent and small quantities of oil insoluble sulphonates. The hydrophobe extract in column 5 which now contains almost pure truly oil soluble sulphonates of the highest detergent and emulsifying qualities proceeds through line 7 to an evaporator as shown in Figure 1 where the hydrophobe solvent is vaporized and a substantially pure truly oil soluble mahogany salt is recovered.

The wash water in column 5 is withdrawn through line 9. A portion or all of it is preferably returned through line 10 to the top of column 2, to aid in the separation of the sulphonates, whereby yields and purity of the true sulphonic compounds are increased. Wash water not returned to column 2 may be withdrawn through line 8 together with the hydrophile extracted solution from column 2. Green sulphonic compounds contained in the latter may be recovered by known methods, such as salting out or evaporation.

While I have described a particular method of producing and handling the sulphonic compounds it shall be understood that this method is merely illustrative. For instance, the neutralization in treater II may be omitted or be carried out at a later stage, and at least one of the extractions in extraction units I to III may be carried out in the acid condition. However, to avoid corrosion difficulties and because of more efficient separation due to the fact that the less desirable free sulphonic acids are somewhat more soluble in hydrocarbon oils than their salts, it is usually preferred to neutralize the oil or make it slightly alkaline at the earliest opportunity.

The de-oiling step in extraction unit II, while very desirable, is not essential in my process. Failure to remove entrained or dissolved mineral oil will cause the desired truly oil soluble sulphonic compounds to be contaminated therewith after removal of the hydrophobe solvent. If desired, a separation of the desired product and oil may be carried out by extracting the hydrophobe solution with an aqueous hydrophile solvent of the type described under conditions to transfer substantially all sulphonic compounds contained in the former to the hydrophile solvent while leaving the mineral oil in the hydrophobe solvent. The purified sulphonic compounds may then be recovered from the hydrophile solution by evaporating the solvent therefrom.

Instead of starting my process with mineral oil and sulphuric acid, I may begin with prepared mahogany salts such as commercial mahogany salts, which usually contain from about 20 to 30% mineral oil, up to 5% of sulphate, up to 10% of naphthenic and fatty acid soaps, varying percentages of moisture, and a remainder which consists of varying proportions of truly oil soluble and difficultly oil soluble sulphonates. The content of the truly oil soluble sulphonates in the remainder is usually between the approximate limits of about 30 to 70%. Preferably, I first dissolve the mahogany salt in an aqueous organic hydrophile solvent. The resulting solution may then be de-oiled and the de-oiled solution is extracted with a hydrophobe solvent as described. As hereinbefore explained de-oiling as a separate step, may be omitted, particularly if a hydrophile solvent is used for dissolving the salt which has a low solvent capacity for mineral oil in the presence of dissolved sulphonates, such as 85% aqueous ethylene glycol, and which permits separation of at least a portion of the oil from the resulting hydrophile solution by settling or centrifuging; or de-oiling may be carried out by re-extracting the salt in the hydrophobe solution with a hydrophile solvent, as described.

Other impurities such as naphthenic and fatty acid soaps as well as sulphates being preferentially soluble in hydrophile solvents are little extracted by hydrophobe solvents and do not contaminate to any extent the hydrophobe solution of the desired sulphonic acids or salts.

As an alternative procedure a commercial mahogany salt may be dissolved in a suitable hydrophobe solvent and the resulting solution is treater preferably in counterflow with an aqueous organic hydrophile solvent under conditions to extract only that portion of the salt which is least soluble in hydrocarbons and to leave the true oil soluble salt in the hydrophobe solvent.

The yields of true oil soluble sulphonic acids or salts obtainable by my process obviously depend primarily on the composition of the oil soluble acid or salt mixture. In a particular instance, a commercial mahogany salt of the following composition was subjected to my process:

	Per cent
Water	10.2
Mineral oil	25.0
Naphthenic and fatty soaps	9.8
Sodium sulphonate	51.0
Sodium sulphate	4.0
Total	100.0

This salt was dissolved in aqueous 85% ethylene glycol to make a salt solution of about 20%. The resulting solution was washed twice with about 20% by volume petroleum ether to remove mineral oil and the remaining solution was then thoroughly extracted with toluene. The toluene extract after evaporation to dryness amounted to 35% by weight of the original mahogany salt. It was completely soluble in all mineral oils including paraffinum liquidum, had excellent detergent qualities, and produced very stable emulsions which did not separate appreciably after several days of standing.

The sulphonates remaining in the glycol were then recovered by acidifying the solution and extracting it with a large volume of petroleum ether. Sulphonic naphthenic and fatty acids were dissolved in the petroleum ether and separated from sulphuric acid. The petroleum ether solution was then re-extracted with 50% aqueous alcohol to dissolve sulphonic acids and to separate them from naphthenic and fatty acids. The alcohol solution was neutralized and evaporated to dryness yielding 16% of a sulphonic acid salt which was insoluble in hydrocarbon oils, had poor detergent qualities, and produced emulsions which rapidly settled out.

In the following table the emulsifying qualities of the original mahogany salt and the two salt fractions obtained therefrom are compared. The emulsifying test consisted of dissolving 10 grams of the salt to be tested in 90 grams of a white medicinal oil, shaking 10 milliliters of the resulting solution with 90 milliliters of distilled water in a mechanical shaker for three minutes,

allowing the mixture to stand, and noting its condition at various time intervals.

Origin of the sulphonate used	Original mahogany commercial salt	Toluene soluble salt fraction	Toluene insoluble salt fraction
Original condition of the emulsion.	White milky emulsion	White milky emulsion	Hardly any emulsion at all.
After 12 hours	Cream appears on top	Homogeneous throughout	Complete separation after 5 minutes.
After 24 hours	1.1 ccs. of cream on top	0.2 cc. of cream on top.	
After 48 hours	No oil has separated in this emulsion. Aqueous layer has become somewhat more transparent.	No oil has separated in this emulsion. Aqueous layer is still very opaque.	
After 72 hours	Cream 1¼ cc. Dark emulsion 0.6 cc. thick. Aqueous layer has become more transparent. No oil separation.	Cream 1¼ cc. Homogeneous opaque. No oil separation.	
After 96 hours	Minute drops of oil have separated in this emulsion.	No oil separation.	
After 144 hours	Cream on top 1¼ cc. then ½ cc. of milky emulsion. The remaining emulsion is thin, translucent and brownish. Drops of oil on top.	Cream on top 1¼ cc. Remaining emulsion is milky white as initial emulsion. No oil has yet separated.	

While in the foregoing I have described the fractionation of oil soluble sulphonic compounds of the type derived by sulphuric acid treatment of certain hydrocarbon oils, it shall be understood that my method is also applicable to the fractionation of other oil soluble sulphonic compounds such as may be derived from certain fatty oils and/or fatty acids.

I claim as my invention:

1. In the process of separating components of relatively high detergent and emulsifying properties from an oil-soluble substantially oil-free mixture of sulphonic compounds having varying detergent and emulsifying properties and solubilities in hydrocarbon oils, the steps comprising subjecting said mixture to the action of two counter-flowing mutually substantially immiscible organic solvents a water-insoluble solvent, separable from sulphonic compounds by distillation, and a water-soluble solvent, under conditions to form two liquid phases with a different solvent predominating in each phase and each phase containing a portion of sulphonic compounds of different composition from that of the other portion, separating the liquid phases and distilling the phase with predominating content of the water-insoluble solvent to separate and recover the sulphonic compounds dissolved therein.

2. In the process of separating components of relatively high detergent and emulsifying properties from a substantially oil-free mixture of sulphonic compounds having varying detergent and emulsifying properties and solubilities in hydrocarbon oils, obtained by sulphonating a hydrocarbon oil boiling above kerosene, the steps comprising subjecting said substantially oil-free mixture to the simultaneous solvent action of two mutually substantially immiscible solvents, one of which is a water-insoluble solvent separable from sulphonic compounds by distillation and another is a water-soluble solvent, under conditions to form separate liquid phases, one containing substantial portions of the water-insoluble solvent and sulphonic compounds readily soluble in hydrocarbon oils and possessing relatively high detergent and emulsifying properties, and another one containing the water-soluble solvent and the sulphonic compounds less readily soluble in hydrocarbon oils, separating the phases and distilling the first phase to separate and recover the sulphonic compounds contained therein.

3. In the process of separating components of relatively high detergent and emulsifying properties from a substantially oil-free mixture of sulphonic compounds having varying detergent and emulsifying properties and solubilities in hydrocarbon oils, obtained by sulphonating a hydrocarbon oil boiling above kerosene, the steps comprising dissolving said substantially oil-free mixture in an organic water-soluble solvent in which the mixture is soluble and extracting the resulting solution with a water-insoluble solvent which is separable from sulphonic compounds by distillation and substantially immiscible with the water-soluble solvent, under conditions to form separate liquid phases, one containing substantial portions of the water-insoluble solvent and sulphonic compounds readily soluble in hydrocarbon oils and possessing relatively high detergent and emulsifying properties, and another one containing the water-soluble solvent and the sulphonic compounds less readily soluble in hydrocarbon oils, separating the phases and distilling the first phase to separate and recover the sulphonic compounds contained therein.

4. In the process of separating components of relatively high detergent and emulsifying properties from a substantially oil-free mixture of sulphonic compounds having varying detergent and emulsifying properties and solubilities in hydrocarbon oils, obtained by sulphonating a hydrocarbon oil boiling above kerosene, the steps comprising dissolving said mixture in an organic water-soluble solvent in which the mixture is soluble, subjecting the resultant solution to an extraction of counter-flowing water and an organic water-insoluble solvent separable from the sulphonic compounds by distillation, the water-soluble and water-insoluble solvents being substantially immiscible with each other in the presence of said sulphonic compounds, under conditions to form two layers each of which contains a material fraction of sulphonic compounds originally contained in the mixture, separating the layers and distilling the water-insoluble layer to separate and recover the sulphonic compounds dissolved therein.

5. The process of claim 2 in which the water-insoluble solvent is an aromatic hydrocarbon solvent.

6. The process of claim 2 in which the water-insoluble solvent is toluene.

7. The process of claim 2 in which the water-soluble solvent contains an amount of water to render it substantially immiscible with the water-insoluble solvent.

8. The process of claim 2 in which the mixture comprises alkali metal sulphonates.

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