MANUFACTURE OF SULFONATES FROM PETROLEUM OILS

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This invention relates to processes for manufacturing hydrocarbon sulfonates, more especially oil-soluble sulfonates from petroleum hydrocarbons such as those commonly obtained from petroleum fractions of the lubricating oil type, particularly those derived from the well-known naphthenic petroleum oils.

A general object of the invention is to provide an improved and comparatively simple method for producing petroleum sulfonates of metals for use in motor oils and for other compounded lubricants and other uses.

It is further an object to produce oil-soluble petroleum sulfonates of the indicated nature which have been purified in a manner to exclude from them salts of the well-known "green sulfonic acids" which are objectionable for most uses, and to leave relatively pure "magnesium sulfonates" which constitute the products desired and which are preferentially oil-soluble.

It is also an object of the invention to proceed with the production of the desired sulfonates by a way of initially produced crude ammonium sulfonates, rather than by way of more common procedures involving initially producing crude sulfonates of one of the alkali metals, more especially sodium sulfonates.


I have discovered that processing methods involving initial production of ammonium sulfonates from conventionally prepared or other crude sulfonic acids from petroleum fractions render operations procedure much more simple, than do alkali metal sulfonate methods, in moving from the crude sulfonic acids to the oil-soluble water-insoluble petroleum sulfonates of polyvalent metals, which are the preferred form of product for a great many uses. These include particularly the alkaline earth metal sulfonates, namely barium, magnesium and strontium sulfonates.

In the sulfonation of petroleum lubricating fractions, and the like, as above indicated, there are always produced, along with the preferentially oil-soluble "mahogany sulfonic acids" a small but objectionable quantity of so-called "green sulfonic acids", which are preferentially water-soluble. If not carefully eliminated, they carry along with the mahogany sulfonic acids and their sulfonates in solution in the accompanying oils, and exert their characteristic objectionable influences in the mahogany sulfonate products, such as settling and cloudy formation, and interference with corrosion protection in the presence of moisture.

By the present process, employing ammonium sulfonates, these small proportions of objectionable green acid sulfonates are quite readily eliminated. Also, when it comes later to the production of the desired polyvalent metal sulfonates mentioned, the conversion of the ammonium sulfonates to polyvalent metal sulfonates, e.g. calcium sulfonate which will be usually considered herein as representative of the group, and the separation of these sulfonates from brines and sludges encountered and from excess oil carrying over from the original crude sulfonic acids, are very greatly simplified over most other conversion and separation procedures; and the resulting products are of higher quality for many purposes, particularly for use in anti-rust oils where freedom from chloride ions is very desirable.

Sulfonation of the indicated petroleum fractions, such as lubricating oils from aromatic-type petroleum having a molecular weight in the range of about 400 to 550 may be effected in any well known or preferred manner. Thus, characteristically such oils, at one stage of their refining, are treated with strong sulfuric acid or conventional fuming sulfuric acid containing for example about 25% oleum, such acid otherwise being termed 106% H$_2$SO$_4$. A ratio of 2 to 3 pounds of such fuming sulfuric acid to each gallon of oil is characteristic. Temperatures are controlled in well known manners to avoid overheating, such as not to exceed about 140° F., and thereby avoid over-treatment or destruction of desired sulfonic acids.

Reference is made to the accompanying flow sheet which illustrates the various steps of the present process, and in which conventional sulfonation as just above described is indicated by a sulfonation system 10 from which the resultant acid sludge is discharged by way of line 11. The unsulfonated oil and contained sulfonic acids are transferred from the sulfonation stage to a neutralization apparatus 12 for the formation of ammonium sulfonates from the sulfonic acids contained in the oil. Such production of ammonium petroleum sulfonates is readily accomplished by any known or preferred procedure requiring introduction of ammonia, in the form of ammonium hydroxide for example, through a line 14 into the oil and sulfonic acid mixture with adequate commingling thereof to effect neutralization reactions. A moderate excess of ammonia is desired to insure complete neutralization.

Such a crude ammonium soap (sulfonate) in the "unsulfonatable" oil may constitute the starting material for production of the oil-soluble mahogany ammonium sulfonates of alkaline earth metals in accordance with this invention. Such a crude product from the neutralization step may contain typically about 100 parts by weight of the sulfonate, around 400 parts by weight of the unsulfonated or "unsulfonatable" oil, together with 5 to 20 parts by weight of water, and around 4 to 10 parts by weight of inorganic salts, such as ammonium sulfates and sulfites. Thus, a typical soap stock might contain 70% to 80% of unsulfonated oil, 15% to 20%, e. g. 18%, of amonium sulfonates; 5% to 10% of water usually containing some excess ammonia; and 2% or 3% of the mentioned inorganic salts.

With respect to the sulfonic acids, whose indicated metal salts are to be produced for use in lubricating oils, other compounded lubricants, rust-preventing compounds, and the like, as is well known a large proportion of these sulfonic acids is oil-soluble acids known as "mahogany acids" which are found in solution in a supernatant oil layer accumulating above the acid sludge layer upon settling of the batch of sulfonated lubricating oil, or other indicated fraction, following strong sulfonic acid treatment yielding the sulfonic acids. However, the sulfonic acid treatment of these oil results also in the production of other sulfonic acids which are known as "green acids" and are primarily or preferentially water-soluble, such green acids being therefore found chiefly in the acid sludge layer. However, some of these water-soluble green acids are nevertheless found in the presence of the
oil-soluble mahogany acids in the oil layer and are objectionable for many purposes. Possibly these vaurant
water-soluble sulfonic acids pass into the oil layer be
cause they are at the same time moderately oil-soluble, or
because they are to that extent solubilized by the action
of the mahogany acids, or because of the failure to re
move the last traces of "pepper sludge" from the acid-
treated oil. As a result, these objectionable water-
soluble green acids which are carried over into the oil
layer with the mahogany acids appear in the crude sul
fonic acid product constituting the oil layer. Usually
such product is treated with sodium hydroxide and placed
on the market as crude sodium mahogany sulfonates in
oil, carrying nevertheless the contaminating green acid
sulfonates. Commonly the sodium salts are converted
by metalization to alkaline earth metal sulfonates, all of
which are readily oil-soluble, or at least the green acid
sulfonates are oil-soluble in the presence of the mahogany
acid sulfonates. But the green acid alkalai metal sul
fonates are also water-soluble, and because of this water
solubility they are objectionable in lubricants and rust-
preventives where moisture might be encountered, imas
duced a weak resistance to water of an oil film on metal and permit rusting to occur.

A further important object of the present invention is therefore to prepare ammonium mahogany sulfonate and to purify such ammonium mahogany sulfonate by ridding them of the objectionable green acid sulfonates. Also it is desired to purify the mahogany sulfonates by eliminating the mentioned inorganic sulfates and other inorganic salts which would later form oil-insoluble alka
line earth metal salts.

Since subsequent treatment of the original crude sul
fonates in oil to convert them to oil-soluble polyvalent
metal sulfonates such as calcium sulfonates has hereto
fore often resulted in difficulty breaking emulsions formed
in conjunction with the conversion, it is therefore an
other object of this invention to provide a process to
avoid such refractory emulsion conditions by working with
ammonium sulfonates and converting them to the desired
polyvalent metal sulfonates, by use of appropriate oxides
or hydroxides, such as lime slurries, whereby to avoid
introduction of corresponding acid ions which are usually
very objectionable.

Thus, various objects of the invention are, in brief: to
eliminate all green acid sulfonates from the mahogany
acid sulfonates; to eliminate all objectionable inorganic
salts readily; to eliminate excess oil from the sulfonates
so as to yield readily a sulfonate concentrate, and parti-
cularly to remove excess oil before conversion of the ma
hogany sulfonates to the water-insoluble polyvalent metal
form; and to provide a process adaptable to crude am
monium sulfonates containing high percentages of mineral
oil, such as 70% to 85% mineral oil, considerable pro-
portions of water, and even very small proportions of in
organic salts, as well as small proportions of green acid
sulfonates.

Throughout this specification, where the term "soap"
is employed, it is intended to signify the respective sul
fonate. Where the term "concentrate" or equivalent is
employed, last significance is a higher proportion of sul
fonate to the oil present than in the starting material.
Where the term "water-soluble" or the term "oil-soluble"
is used, such term generally signifies relative solubility or
miscibility in water or oil as the case may be, unless other
meaning is fairly indicated. Where reference is made to
removal or elimination of green acid soaps and inorganic
salts, such terminology is intended to include either com-
plete elimination or a reduction of the respective materials
to such insignificant proportions that the presence of the
remainder does not interfere seriously with subsequent processes and is not detrimental to the uses to which
the sulfonate product is eventually to be put.

Purification

Referring again to the accompanying flow sheet, sul
fonation of the oil feed stock is indicated together with
neutralization with ammonia of the separated unsul
fonatable oil and sulfonic acids dissolved therein.

Thus, the crude ammonium sulfonate-in-oil solution
produced in the neutralizing apparatus 12 is transferred
to a treating apparatus 15 into which an emulsifying
liquid, which may be referred to as a "solvent," is supplied
by a line 16 and also into which additional water if re
quired (which may be a common salt solution containing
for example about 5% NaCl) may be supplied by a line
17. The apparatus 15 may include such heating means 18
and mixing means 19 as necessary for uniform mixing and
complete dispersion to provide a mixture easy to pump and susceptible to good subsequent stratification.

The resultant mixture of the crude ammonium sul
fonate-in-oil with the indicated solvent and the indi-
cated water, if required, is then pumped to a suitable
settling tank 20, wherein, normally, the solvent-treated
batch will stratify to yield an upper oil phase, an inter-
mediate purified ammonium sulfonate-in-oil containing
substantial quantities of the solvent, and a brine phase
containing water, ammonium sulfate and the solvent in
stantially all of the green acid sulfonate. As indicated,
the brine layer may be withdrawn from the settling tank
20 by a line 21 and passed to treatment for recovery of
excess ammonia and contained solvent, lime or caustic
soda being added to completely liberate NH3. The upper
oil phase may be withdrawn through a line 22 to a stripper
23 for separation of solvent and ammonia dissolved there-
in, the stripped oil being then passed by a line 24 to oil
storage 25 via a filter 26 or to other apparatus for any
desired additional treatment and appropriate subsequent
use. Lime can be added at 22r to convert any am
monium soap remaining in the oil.

The intermediate phase shown in the settling tank 20,
which consists of the purified ammonium sulfonate in
oil with substantial quantities of solvent, after adequate
stratification, is ready for subsequent treatment with
a polyvalent metal compound to convert the ammonium
sulfonate to the metal sulfonate, more particularly an
alkaline earth metal sulfonate, such as calcium sulfonate.

The required purification of the stratified ammonium
sulfonate-oil layer in the settling tank 20 is accomplished
through the agency of the particular type of solvent in-
troduced into the apparatus 15 through the line 16, and
the amount of oil separated as the oil phase in the top
of the settling tank 20 is controlled through the agency,
not only of such solvent, but of water introduced through
the line 17.

Respecting the solvent or emulsion-breaking liquid, this
is, under the conditions of use, an organic liquid which
is at least partially water-soluble, consists of carbon, hy
drogen and oxygen, has a boiling point suitably low to
facilitate its removal and recovery from the various
phases, and has sufficiently low operating viscosity not to
disturb seriously the various operations. Its boiling point
is preferred to be below the decomposition point of the
sulfonates so that this diluent liquid may be readily elimi
nated from the sulfonate product by vaporization. This
signifies a boiling point generally not in excess of 400°
F., inasmuch as the initial decomposition temperature
of a sulfonate such as calcium sulfonate may be in the
neighborhood of 450° F. to 500° F. Otherwise, with the
higher boiling solvents recovery should be by distillation
under vacuum.

Such an emulsion-breaking liquid solvent will be se
lected from a large class consisting of alcohols, ethers,
gerbers, glycols, and ketones, containing from 3 to 8
carbon atoms per molecule. The alcohols, which may
be considered a preferred group, usually are the butyl
alcohols, such as secondary butyl alcohol (SBA) which
is usually preferred, and also normal and tertiary butyl
alcohols; the amyl alcohols, such as secondary amyl
alcohol but also primary and tertiary amyl alcohol and
isoamyl alcohol; and the various hexyl alcohols, including normal hexyl alcohol, ethyl propyl carbinol, methyl isobutyl carbinol, methyl n-butyl carbinol, and so on. All these alcohols, like the isomers of amyl alcohol, have a carbon to oxygen ratio not higher than 4 atoms of carbon to 1 atom of oxygen, such as represented by the above examples, of which the preferred member is methyl ethyl ketone. As to ethers falling within the above definition and containing from 4 to 6 carbon atoms per molecule, usable examples are the following: ethylene glycol dimethyl ether, ethylene glycol monoamyl alcohol, diethylene glycol dimethyl ether, ethylene glycol ethyl ether, and ethylene glycol methyl ether acetate. All of these bear the carbon to oxygen ratio of approximately 2 to 1, and the preferred member for the present purpose is ethylene glycol monobutyl ether (otherwise known as butyl "Cellosolve"). Respecting the glycols falling within the above definition, examples thereof are the following: diethylene glycol, dipropylene glycol, hexylene glycol, and butylene glycol. Respecting esters within the above definition, examples are: ethyl acetate; propyl acetate; isopropyl propionate; propyl acetate, propyl formate and ethyl formate.

I have discovered that by introducing appropriate amounts of an emulsion-breaking oil-soluble solvent, such as above described, with appropriate proportions of water, the objectionable inorganic salts and the mentioned green acid sulfonates are rejected in the brine phase which settles out of the bottom layer upon standing, as above described. Very large gallonages of these materials may be readily handled so that treatment may be on a very large scale. I have also discovered that "excess oil," such as represented by the above-mentioned oil-liquid phase rising in the top of the settling tank 20, may be separated, upon settling, from the above-mentioned ammonium sulfonate-in-oil layer by fairly well controlled proportions of water and emulsion-breaking liquid solvent, such proportions being determined in accordance with the amount of the soap oil content of the crude sulfonate. Thus, in general, by establishing the proportion of emulsion-breaking liquid solvent at a relatively low level, such as between 4 and 5 volumes per 100 volumes of the soap-oil mixture in the crude ammonium sulfonate-oil solution, and then adding water in gradually increasing amounts, a brine phase first appears which settles to the bottom and may be drawn off. Then, by making further additions of water, an oil phase may also be made to appear, which oil phase rises to the top, whereby to leave the previously described intermediate ammonium sulfonate-in-oil phase. If desired, appropriate amounts of emulsion-breaking liquid solvent and of water may be introduced into the pump apparatus 15 to the separation in the settling tank 20 of such proportion of oil in the upper layer as may be desired. Or, no more water would be introduced into the apparatus 15 than required for the rejection of the brine phase. The amount of water may, of course, vary with stocks, as may the amount of emulsion-breaking solvent, but in general at least 10 parts by volume of water are required per 100 parts by volume of the hydrocarbon oil-sulfonate solution, and as above indicated, at least 5 parts by volume of emulsion-breaking liquid per 100 volumes of the soap oil solution are required. The range of the emulsion-breaking liquid has been indicated above, and the range of water will normally vary between about the mentioned 10% and 60% in accordance with the amount of oil "desired" to be rejected in a concentration step. In general at least 20% of water is desirable with at least 10% of emulsion-breaking solvent. Often, it is desirable to have present at least enough solvent to saturate or approximately saturate the oil to get good separation. This is true especially where high volume ratios of water (e.g. 40% to 60%) based on the oil-sulfonate content are used. Otherwise, good solvent contents are found in the range of 10% to 50% of the total water content, or within a range of about 5% to 50% based on the oil-sulfonate content. The economically and operatively preferred range is from 15% to 40% of emulsion-breaking solvent, based on the oil-sulfonate content. As to soap-oil mixtures susceptible to the present treatment, oil contents may drop to 25% oil and sulfonate contents may increase to 75% oil, with anywhere from about 1/2% to 3% of green acids soaps and around 1/4 to 4% or more of inorganic sulfates and sulfites based on the soap-oil mixtures. Commonly ammonium sulfonates to be treated contain anywhere from about 50% to 90% of oil based on the oil-soap mixture, or in other words from about 50% down to 10% soap.

Concentration

In connection with the addition of increased amounts of emulsion-breaking liquid or water, or both, to increase oil rejection, and corresponding concentration, the brine phase should be removed to avoid its going back into solution upon the further additions of solvent and water to reject further quantities of oil. The percentages and conditions as above given refer principally to treatment with secondary butyl alcohol (SBA) as the emulsion-breaking solvent, but in general they are true of the other solvents indicated.

In view of the tendency to redissolve the brine phase when additions of solvent and water are made to increase oil rejection, it is usually preferable to consider an purification step (oil separation) separately from the concentration step (oil separation). It is, however, possible to produce both a brine layer containing the inorganic salts and green acid soaps, and a rejected oil layer containing excess oil, in one step, somewhat as indicated in the settling tank 20, by careful selection of the treating doses of water and emulsion-breaking liquid.

Therefore, for convenience of operation and greatest flexibility, with less skilled personnel, it is desirable to operate with at least only a small amount of oil rejection at the oil phase of settling tank 20, and rely upon the settling operation in tank 20 as primarily a purification step whereby the brine is separated to eliminate the inorganic salts mentioned and the green acid soaps. Then the desired concentration is effected by passing the ammonium sulfonate-in-oil layer to concentration apparatus 30 via a line 31, which apparatus 30 would, of course, be bypassed if a desired amount of oil rejection had been effected in the settling tank 20, such bypassing being accomplished by a valved extension line 32. When the concentration apparatus 30 is to be employed, the ammonium sulfonate-in-oil solution, with its contained water inactivating and solvating, is passed to the apparatus 30 via a valved branch line 33. The apparatus 30 is much like the apparatus 15 and receives additional water through a charging line 34 and additional solvent through a charging line 35 as may be required. After treatment and strati- fication, the rejected oil phase which accumulates in the top of the tank of the apparatus 30 may be discharged through a line 36 to the stripper 23 and thence to the storage tank 25 along with any oil phase which may have been removed from the settling tank 20. The concentrated soap-oil phase is withdrawn by valve line 37 and passed to the concentrate line 38 by which it is conducted to soap conversion apparatus 40.

Conversion

The soap-oil concentrate in the conversion apparatus
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40, now freed from excess oil, objectionable inorganic salts and green acid sulfonates, is commingled with an appropriate basic metal compound, commonly a calcium compound, and typically a lime slurry, whereby to yield calcium sulfonate. If one of the other alkaline earth metal sulfonates is required, such as barium or strontium, a corresponding compound thereof would be used. Dry metal oxide or hydroxide can be added, but a water slurry, such as the mentioned lime slurry, is preferred, the desired hydroxide being readily supplied by way of the oxide. This is sometimes convenient to hold the metal oxide as a slurry in oil, e. g. lubricating oil.

For the purpose of the following disclosure, the production of calcium sulfonate will be taken as an example, and the preferred lime slurry will be the basic metal compound considered.

For the purpose of supplying the lime slurry to the soap-oil concentrate to effect conversion to calcium sulfonate, such lime slurry is shown as being introduced in appropriate proportion from a line 42 into the concentrate line 32 whence the mixture is conducted to any preferred or required mixer and heater combination 44 in the conversion zone 40 to insure adequate contact and reaction to convert the soap to a calcium sulfonate, this mixture then passing by a line 45 to a stripper 50.

The lime slurry is, of course, adequate to convert all of the ammonium sulfonate and yield corresponding calcium sulfonate which is soluble in the oil of the concentrate. In the stripper 50 the ammonia present and the solvent are boiled off and passed by a line 52, to a suitable condensing apparatus 54 and appropriate ammonia and solvent recovery and storage 55. Such recovery apparatus 55 may also receive corresponding gases and vapors from the previously mentioned stripper 23 by way of a vapor line 52a and condenser 54a. Steam can be introduced into the column 50 by a line 56 if desired to facilitate volatilization.

The stripped converted soap-oil concentrate, which in the situation described is calcium sulfonate in the accompanying oil, at a temperature of 300° F. or above, is removed from the stripper 50, passed to a filter press or other separating means 58 for the removal of such residual solids as might be present and excess lime, such filtered purified concentrate of oil-soluble polyvalent metal sulfonate in oil being then transferred to appropriate storage 60 to constitute the converted product of this invention. Where desired, or required in the case of a product for a particular use, soap-free oil from the oil storage 25 and soap-oil concentrate from the sulfonate product storage 60 may be passed in metered quantities via lines 62 to a blending tank 64.

It will be appreciated that, when desired, oil-soluble sulfonates of other polyvalent metals may be produced by conversion of the above-described ammonium sulfonates with appropriate metal oxides or hydroxides, of which metals zinc, aluminum, lead, cadmium and molybdenum are representative. Sulfonates of the higher boiling amines such as morpholine and dibutyl amine can also be made in this manner by heating the ammonium sulfonate in oil solution with the free amine. It should be appreciated that should the rejected oil phase from either the settling tank 20 or the concentration apparatus 50 contain any small proportion of ammonium sulfonate, such oil may be treated with a lime slurry or equivalent, added by line 22a, to convert such small amount of ammonium sulfonate to calcium sulfonate or the like.

EXAMPLES

The following examples will serve to illustrate my process of making ammonium sulfonate and converting to alkaline earth metal sulfonate.

**Example 1**

A heavy benzene alkylate bottom stock having a molecular weight of about 400 was sulfonated with 26% oleum in two stages, settling sludge between treatments. The sulfonated oil was a heavy, viscous product containing about 60% to 70% of sulfonic acids along with sulfuric acid and dissolved SO3. One hundred parts by weight were added gradually with agitation to excess ammonium hydroxide (28% NH3). Reaction stabilization gave a yellow emulsion or jelly. The concentration was reduced by adding 100 parts of 60 viscosity pale oil; then 90 parts of dioxane and 150 parts of water were added with thorough mixing. About 10 parts of ammonium acetate in water were added to assist separation of an aqueous phase and the mixture was settled at 150° F.

The aqueous phase which separated (142 parts) contained ammonium sulfate and sulfate as shown by tests, as well as water-soluble ammonium sulfonates.

The oil phase, 380 parts, was dehydrated with 15 parts of lime to convert the ammonium sulfonate to calcium sulfonate. Presence of excessive amounts of calcium acetate necessitated further washing of the sulfonate with water and a small amount of butyl alcohol as an emulsion preventer. The oil was then dehydrated to 300° F. and filtered, yielding 165 parts of a very fluid, dark red-brown oil. Analysis showed: alkali value—ASTM—6.5; ash—sulfated—7.38%.

**Example 2**

Two hundred parts by weight of the same sulfonated oil described in Example 1 was neutralized with excess NH4OH (28% NH3), diluted with 200 parts of 60 pale oil, and then mixed with 200 parts of water and 100 parts of secondary butyl alcohol saturated with water (70%). After settling at 140° F., a brine layer of 55 parts was withdrawn. When the brine was acidified, copious amounts of SO2 were evolved indicating removal of sulfate in the brine. Addition of BaCl2 precipitated 1.5 parts of barium sulfate equivalent to 0.85 part of ammonium sulfate removed in the brine.

A second extraction with 50 parts of water, 25 parts of NH4OH (28% NH3) and 25 parts of acetic acid resulted in separation of a brine layer of 180 parts, leaving 500 parts of clear oil which was dehydrated with 25 parts of lime to convert the ammonium sulfonate to calcium sulfonate. At 400° F. the oil and sulfonate was filtered with diatomaceous earth filter aid. The yield was 380 parts of clear sulfonate which gelled on cooling, due to some calcium acetate content. Analysis gave: alkali value—ASTM—9.5; ash—sulfated—8.46%.

**Example 3**

A solvent extracted lubricating oil of about 450 molecular weight was sulfonated with 20% by weight of oleum (26%) and settled to remove sludge. To 100 parts of concentrated ammonium water was added 250 parts of the acid oil separated from sludge. The sulfonic acids and contaminating sulfuric and sulfurous acids were rapidly neutralized, giving a clear yellow emulsion. To this was added 100 parts of dioxane, followed by settling at 150° F. A brine layer, 50 parts, was removed and analyzed for sulfate after acidifying and expelling SO2. Ammonium sulfate in the brine amounted to 0.9 part by weight.

A second extraction with 100 parts of water and 50 parts of dioxane gave a brine layer, on settling, of 120 parts.

The oil layer, 244 parts, was converted to barium sulfonate by dehydrating with 30 parts of barium oxide, after which it was filtered with "Hy Flo" diatomaceous earth. Analysis gave: alkali value—ASTM—11.2; ash—sulfated—6.71%.

The invention claimed is:

1. A process of preparing oil-soluble sulfonates from hydrocarbon oils, including: treating a mineral lubricating oil fraction with strong sulfuric acid, thereby yield-
9 ing a solution consisting principally of large proportions of hydrocarbon oil and mahogany acids and appreciable green acid; removing acid sludge from the solution; treating such solution with ammonia to form ammonium mahogany sulfonates and ammonium green acid sulfonates containing small amounts of inorganic sulfates and sulfites; forming a liquid mixture consisting essentially of said oil, sulfonates, sulfates, and sulfites, at least 10 parts by volume of water per 100 parts by volume of said oil and sulfonates combined, and at least 5 parts by volume per 100 parts by volume of said oil and sulfonates combined of a partially water-soluble, hydrocarbon-oil-soluble oxygen-containing emulsion-breaking solvent compound in liquid form soluble in the oil in the presence of the water and containing three to eight carbon atoms per molecule and selected from the class consisting of alcohols, ketones, ethers, esters and glycols, the amounts of water, oil and organic solvent producing at least two separable phases including a water phase and an ammonium sulfonate-in-oil phase; and separating and recovering said ammonium sulfonate-in-oil phase.

2. A process as in claim 1, including: heating said ammonium sulfonate-in-oil phase containing said solvent with a basic metal compound to convert said sulfonates to oil-soluble basic metal sulfonates; evaporating ammonia, water and solvent and recovering the resultant oil and dissolved metal sulfonate.

3. A process as in claim 2 wherein the basic metal compound is calcium hydroxide.

4. A process as in claim 2 wherein the basic metal compound is barium hydroxide.

5. A process as in claim 2 wherein the basic metal compound is magnesium hydroxide.

6. A process as in claim 1 including; heating said ammonium sulfonate-in-oil phase containing said solvent with an aqueous dispersion of a polyanivalent metal hydroxide yielding sulfonates insoluble in water and soluble in the oil; and recovering the resultant oil and dissolved sulfonate.

7. A process as in claim 6 wherein the metal is calcium.

8. A process as in claim 6 wherein the metal is barium.

9. A process as in claim 6 wherein the metal is magnesium.

10. A process as in claim 2 including adding additional water and solvent to said sulfonate-in-oil phase to reject a portion of oil before conversion of the sulfonates.

11. A process as in claim 6 including adding additional water and solvent to said sulfonate-in-oil phase to reject a portion of oil before conversion of the sulfonates.

12. A process as in claim 1 including; adding additional water and solvent to reject an oil phase; and separating said water phase with dissolved inorganic salts and said oil phase from said sulfonate-in-oil phase.

13. A process of making oil-soluble sulfonates of metals from petroleum oils, including; sulfonating a mineral lubricating oil fraction to yield an oil containing from about 10% to 50% of sulfonic acids; removing acid sludge from the oil-sulfonic acids solution; neutralizing such sulfonic acids-in-oil solution with excess ammonia, forming ammonium mahogany sulfonates, small proportions of green acid sulfonates, and small proportions of water-soluble inorganic sulfates and sulfites; adding to such sulfonates-in-oil solution at least 10 parts of water per 100 parts by volume of said sulfonates-in-oil solution, and to each 100 parts by volume of said sulfonates-in-oil solution at least 5 parts of a partially water-soluble, oil-soluble oxygen-containing emulsion-breaking solvent compound containing from 3 to 8 carbon atoms per molecule and selected from the class consisting of alcohols, ketones, ethers, esters and glycols and soluble in said oil in the presence of said water, the amounts of water and organic solvent producing at least two separable phases including an ammonium sulfonate-in-oil phase containing said mahogany sulfonates, and a water phase containing said sulfates, sulfites and green acid sulfonates; and separating and recovering said ammonium sulfonates-in-oil phase.

14. A process as in claim 13 including heating said ammonium sulfonate-in-oil phase containing said solvent with an aqueous dispersion of a polyanivalent metal hydroxide to convert said ammonium sulfonates to oil-soluble water-insoluble metal sulfonates, distilling ammonia and solvent therefrom and recovering the resultant oil and metal sulfonates dissolved therein.

15. A process as in claim 14 wherein said polyanivalent metal hydroxide is an alkaline earth metal hydroxide.

16. A process as in claim 14 wherein said polyanivalent metal hydroxide is calcium hydroxide.

References Cited in the file of this patent

UNITED STATES PATENTS

1,930,488 Ramayya Oct. 17, 1933
2,097,440 Blumer Nov. 2, 1937
2,373,793 Sulsie Apr. 17, 1945
2,453,690 Bray Nov. 16, 1948