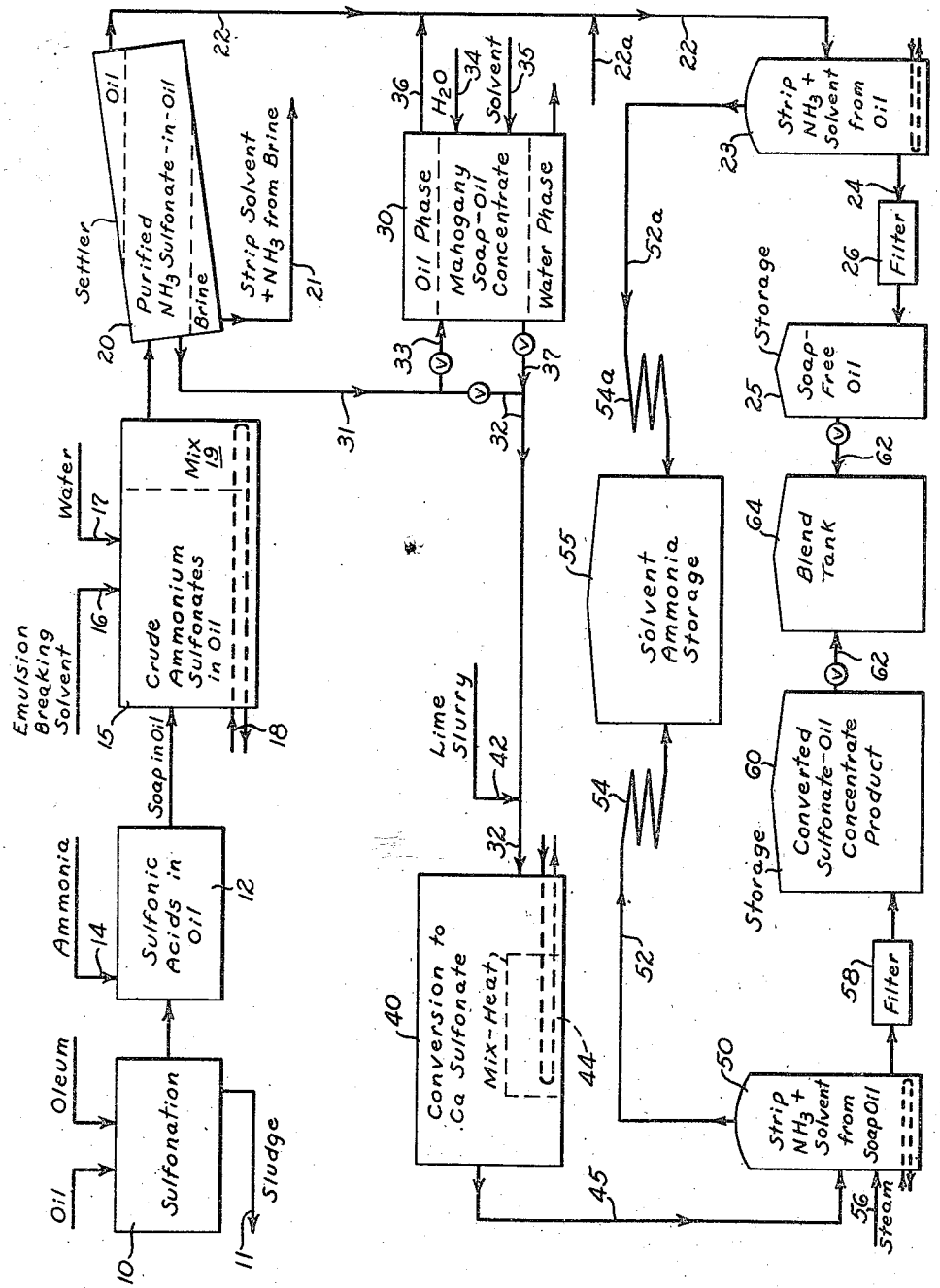
Feb. 18, 1958 U. B. BRAY 2,824,126

MANUFACTURE OF SULFONATES FROM PETROLEUM OILS

Filed April 16, 1956




INVENTOR.
ULRIC B. BRAY

BY HIS ATTORNEYS.
HARRIS, KIECH, FOSTER & HARRIS

United States Patent Office 2,824,126
Patented Feb. 18, 1958



2,824,126

# MANUFACTURE OF SULFONATES FROM PETROLEUM OILS

Ulric B. Bray, Pasadena, Calif., assignor to Bray Oil Company, Los Angeles, Calif., a limited partnership

Application April 16, 1956, Serial No. 578,424

16 Claims. (Cl. 260—504)

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 a further 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 "mahogany 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 way of initially produced crude ammonium sulfonates, rather than by way of more common procedures involving initally producing crude sulfonates of one of the alkali metals, more especially sodium sulfonates.

This application is a continuation-in-part of my earlier applications: Serial No. 309,730, filed September 15, 1952, now Patent No. 2,746,987; Serial No. 442,491, filed July 12, 1954, now Patent No. 2,781,317; Serial No. 442,537, filed July 12, 1954, Patent No. 2,781,316; and Serial No. 442,599, filed July 12, 1954, now Patent No. 2,781,315.

I have discovered that processing methods involving initial production of ammonium sulfonates from conventionally prepared or other crude sulfonic acids from petroleum fractions render operating procedures 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 calcium, 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 gelling and cloud 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% $H_2SO_4$. 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 a 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 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 ammonium 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 sulfuric acid treatment yielding the sulfonic acids. However, the sulfuric acid treatment of these oils 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 vagrant water-soluble sulfonic acids pass into the oil layer because 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 remove 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 sulfonic 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 metathesis 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 alkali metal sulfonates are also water-soluble, and because of this water solubility they are objectionable in lubricants and rust-preventives where moisture might be encountered, inasmuch as they appear to weaken the 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.

It is also an object to purify such mahogany sulfonates by eliminating the mentioned inorganic sulfates and other inorganic salts which would later form oil-insoluble alkaline earth metal salts.

Since subsequent treatment of the original crude sulfonates in oil to convert them to oil-soluble polyvalent metal sulfonates such as calcium sulfonates has heretofore often resulted in difficultly breaking emulsions formed in conjunction with the conversion, it is therefore another 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 particularly to remove excess oil before conversion of the mahogany sulfonates to the water-insoluble polyvalent metal form; and to provide a process adaptable to crude ammonium sulfonates containing high percentages of mineral oil, such as 70% to 85% mineral oil, considerable proportions of water, and even very small proportions of inorganic 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 sulfonate. Where the term "concentrate" or equivalent is employed, the significance is a higher proportion of sulfonate 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 complete elimination or a reduction of the respective materials to such insignificant proportions that the presence of the remainder does not interfere seriously with subsequent processing or is not detrimental for the uses to which the sulfonate product is eventually to be put.

## PURIFICATION

Referring again to the accompanying flow sheet, sulfonation of the oil feed stock is indicated together with neutralization with ammonia of the separated unsulfonatable 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 emulsion-breaking liquid, which is also indicated as a "solvent," is supplied by a line **16** and also into which additional water if required (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 sulfonate-in-oil with the indicated solvent and the indicated 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 intermediate purified ammonium sulfonate-in-oil containing substantial quantities of the solvent, and a brine phase containing water, ammonium salt such as ammonium sulfate and sulfite, some of the solvent in solution and substantially 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 $NH_3$. The upper oil phase may be withdrawn through a line **22** to a stripper **23** for separation of solvent and ammonia dissolved therein, 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 **22***a* to convert any ammonium 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 introduced 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, hydrogen 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 eliminated 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 selected from a large class consisting of alcohols, ethers, esters, 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 alcohols 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 other emulsion-breaking liquids mentioned are oil-soluble and at least partially water-soluble, such as the 12% solubility of the preferred secondary butyl alcohol mentioned.

With respect to the ketone group mentioned, these include acetone, methyl ethyl ketone, diacetone alcohol, acetyl acetone, and acetonyl acetone. The preferred ketones 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 8 carbon atoms per molecule, usable examples are the following: ethylene glycol dimethyl ether, ethylene glycol monobutyl ether, dioxane, diethylene glycol monobutyl ether, diethylene glycol dimethyl ether, ethylene glycol ethyl ether acetate, 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; isopropyl 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 indicated. 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 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 5 and 25 volumes (or sometimes up to 40 to 50 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 purifying apparatus **15** to effect 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 water present, in order 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 70% soap, with anywhere from about ½% to 3% of green acids soaps and around ½ 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 for redissolving the brine phase when additions of solvent and water are made to increase oil rejection, it is usually preferable to conduct the purification step (brine 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 as the oil phase of settling tank **20**, and rely upon the settling operation in tank **20** as primarily a purification stage 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 and solvent, 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 stratification, 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 **32** by which it is conducted to soap conversion apparatus **40**.

*Conversion*

The soap-oil concentrate in the conversion apparatus

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. It is sometimes convenient to add 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 apparatus **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 **52***a* and condenser **54***a*. 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 **30** contain any small proportion of ammonium sulfonate, such oil may be treated with a lime slurry or equivalent, added by line **22***a*, 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 $SO_2$. One hundred parts by weight were added gradually with agitation to excess ammonium hydroxide (28% $NH_3$). Rapid neutralization 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 sulfite 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 $NH_4OH$ (28% $NH_3$), 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 $SO_2$ were evolved indicating removal of sulfite in the brine. Addition of $BaCl_2$ 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 $NH_4OH$ (28% $NH_3$) 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 ammonia 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 $SO_2$. 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-

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 polyvalent 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 polyvalent 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 polyvalent metal hydroxide is an alkaline earth metal hydroxide.

16. A process as in claim 14 wherein said polyvalent 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 | Susie | Apr. 17, 1945 |
| 2,453,690 | Bray | Nov. 16, 1948 |
| 2,727,861 | Brown et al. | Dec. 20, 1955 |