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METHOD FOR PREPARING COMPLEX METAL SALTS OF SULFONIC ACIDS

Ferdinand P. Otto, Woodbury, N.J., assignor to Socony Mobil Oil Company, Inc., a corporation of New York

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This application is a continuation-in-part of application Serial No. 668,031, filed June 26, 1957 and now abandoned.

This invention relates to improved lubricating oil compositions for use in internal combustion engines. More particularly, it relates to a new class of detergent additives for such lubricating oils and to a method for their preparation.

It is well known that lubricating oils tend to deteriorate under the conditions of use in present day diesel and automotive engines with attendant formation of sludge, lacquer and resinous materials which adhere to the engine parts, particularly the piston ring grooves and skirts, thereby lowering the operating efficiency of the engine. To counteract the formation of these deposits, certain chemical additives have been found which when added to lubricating oils have the ability to keep the deposit-forming materials suspended in the oil, so that the engine is kept clean and in efficient operating condition for extended periods of time. These addition agents are known in the art as detergents or dispersants. Metal organic compounds are particularly useful in this respect. These metal organic compounds are considered to be effective on the basis of their metal contents, coupled with their solubility in the oil.

Generally, it has been found that the oil-soluble metal organic compounds having the greater percentages of metal provide the better detergents. On this basis, it has been sought to provide detergent compounds having the highest possible metal content. Metal sulfonates such as metal petroleum sulfonates (obtained by the sulfonation of petroleum oils) and synthetic sulfonates (obtained by the sulfonation of wax aryl compounds, for example—wax benzenes and wax naphthalenes) are recognized in the art as being particularly effective detergents for mineral lubricating oils.

The present invention is concerned with the provision of a new class of metal sulfonates, hereinafter called "complex" metal sulfonates, which have exceptionally high metal contents and which are highly superior oil detergents. The metal contents of these new complex metal detergent salts range from about 100% to about 200% in excess of that obtainable by exact neutralization of the sulfonic acid.

It is an object of this invention to provide a new class of complex metal sulfonic acid salts having exceptionally high metal contents and to provide a method of preparing these salts.

It is a further object of this invention to provide oil compositions containing relatively small amounts of these salts, which compositions are of a high detergent character.

Other and further objects of this invention will hereinafter more fully appear from the following description of this invention.

Broadly, the method of the invention involves the steps of (1) intimately contacting a hydrocarbon solution of a sulfonic acid, in the presence of water, with a metal hydroxide in an amount to supply at least about one equivalent of metal per equivalent of acid-hydrogen present in said sulfonic acid solution, at a temperature of from 25° C. to about 100° C., (2) intimately contacting the reaction mixture from step 1 with formaldehyde and a metal hydroxide, in the presence of water, at a temperature of from about 25° C. to about 100° C., the amount of formaldehyde used being from about two to about four equivalents thereof per equivalent of sulfonic acid in said sulfonic acid solution, and the amount of metal hydroxide present in the reaction mixture along with the formaldehyde being that sufficient to supply at least about two equivalents of metal per equivalent of acid-hydrogen present in said sulfonic acid solution, (3) substantially completely dehydrating the reaction mixture from step 2 and (4) filtering the reaction mixture to remove insolubles.

A satisfactory procedure for carrying out the process of the invention is as follows: An aqueous slurry of the metal hydroxide is first prepared. This slurry is then intimately contacted with the sulfonic acid at a temperature ranging from about 25° C. up to about 100° C. A diluent is required in the case of the synthetic type sulfonic acid in order to facilitate the reaction and the handling of the complex salt product. The synthetic sulfonic acids are, therefore, first dissolved in a hydrocarbon, such as an oil, to form a solution of, say, from about 20% to about 75% of the acid in the oil, this solution being contacted with the reagent slurry. The petroleum sulfonic acids are, of course, already diluted with oil, the acids being present therein in amounts of from 20% to about 75%, and these acids, or sour oils, ordinarily require no addition of other diluent oil for the purpose of the reaction process. The contacting of the sulfonic acid (solution) with the metal hydroxide-water slurry is accomplished by the slow addition of the slurry to the acid solution, or vice versa, with constant stirring so as to assure intimate contacting of the reactants. When the addition is complete, the reaction is digested for a short period, for example, about one-half hour, to insure complete reaction. The formaldehyde (36% solution) is then added slowly to the reaction mixture. When this addition is completed, the reaction mixture is again digested for a period of about thirty minutes. Dehydration of the reaction mixture is then effected by raising the temperature thereof to 110° C. to 120° C. and maintaining this temperature until the dehydration is complete. The dehydrated product is then filtered to remove any excess salt reagent. The product thus obtained is an oil solution which usually contains from about 20% to about 75%, more or less, of the complex salt. It will be appreciated that, in the case of the synthetic type sulfonic acids, other hydrocarbon solvents may be used for the reaction besides mineral oil, such as a light naphtha, xylene, toluene or the like. However, use of a petroleum oil is preferred since it need not be removed after the reaction, the oil solution thus obtained being directly blendable with the lubricating oil, which, ultimately, will be fortified with the complex salt product.

Although the aforedescribed procedure is the one generally used, the manner and time of bringing the sulfonic acid solution and the complexing reagents together may

be varied without markedly affecting the reaction or yield of complex salt product obtained. For example, although the second step of this process would generally be considered as involving the separate addition of a formaldehyde-metal hydroxide "complexing" reagent to the reactants of the first step, it is possible to form this complexing reagent in situ, in which case it is necessary to add only formaldehyde during the second step; this operation can be effected by having present in the initial reaction mixture an excess of the lime-water slurry over and above that required for the formation of the normal salt—then, when the formaldehyde is added, as indicated above, the complexing reagent is formed in situ. On the other hand, and as more generally considered, the initial reaction of the sulfonic acid-lime-water slurry (here preferably containing no substantial excess) may be followed by addition of a complexing reagent comprised of lime, water and formaldehyde. Several different procedures for carrying out the process of the invention are given in the illustrative examples presented hereinafter. In all cases, however, it is essential that a good dispersion of the reactants be obtained, that water be present and that the dehydration be carried substantially to completion.

Due to the intricate nature of the complex metal salts produced by the process of the invention, no chemical formula can be ascribed to them at this time. Neither is the manner of the formation precisely known. It is believed, however, that the complex salts are formed via a two-step process in which the normal metal sulfonate is first formed by reaction with the metal hydroxide, the normal salt then being reacted further with the metal hydroxide-formaldehyde reagent during dehydration to yield the final complex salt product. Since the presence of water is necessary in order to form these complex salts, it appears that ionization is an essential factor in their formation.

With respect to the amount of metal hydroxide and formaldehyde reagents utilized in the process of the invention, it will be appreciated that the formation of the high metal content complex salts requires (a) the reaction of the sulfonic acid (solution) with an amount of metal hydroxide at least sufficient to form a normal salt thereof and (b) the reaction of the said normal salt with a reagent formed from formaldehyde and metal hydroxide, i.e., a formaldehyde-metal hydroxide "complexing" reagent. In carrying out the process of the invention, therefore, it will be appreciated that it is not necessary that the complexing reagent be added as such to the normal salt but may be formed by addition of formaldehyde to the initial metal hydroxide-sulfonic acid reaction mixture containing an excess of metal hydroxide thereby forming the said formaldehyde-metal hydroxide reagent in situ. On the other hand, of course, where an excess of metal hydroxide (over that required to form the normal salt) was not used, additional metal hydroxide must be added along with the formaldehyde reagent.

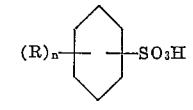
The amount of metal hydroxide to be utilized in step 1 of the process then may range from at least one equivalent per equivalent of acid-hydrogen present in the sulfonic acid solution up to as high as, say, 6 equivalents or higher. Correspondingly, the amount of metal hydroxide to be utilized in step 2 may be from about 1.5 to about 5 equivalents, the metal hydroxide being either added to the reaction mixture from step 1 or comprising metal hydroxide remaining unreacted where an excess of metal hydroxide is employed in step 1. Use of large amounts of metal hydroxide in excess of the aforementioned amounts provide no particular advantage from the standpoint of the amount of metal incorporated into the complex salt product. On the other hand, the use of large excess amounts of metal hydroxide increases the viscosity of the reaction mixture and makes the handling and final filtration of the products more difficult.

The amount of formaldehyde employed in step 2 of the process may be from 2 to 4 equivalents based on the equivalents of sulfonic acid used, 2 to 3 equivalents being preferred.

Formaldehyde and its equivalent, paraformaldehyde, are the preferred aldehydes of the instant process; other aldehydes, such as acetaldehyde, benzaldehyde and furfuraldehyde, yielded sulfonates having metal contents equal to or only slightly higher than those obtained by direct neutralization of the sulfonic acid with a metallic hydroxide.

Although calcium is the preferred metal of this present process, other metals from Groups I and II of Mendeleeff's Periodic Table of the Elements may be employed.

As aforesaid, the sulfonic acids suitable for use in this invention include oil soluble petroleum sulfonic acids and synthetic alkaryl sulfonic acids, particularly those having higher molecular weights, i.e., from about 300 to about 800. These sulfonic acids may be produced by sulfonation of petroleum stocks or synthetic alkyl aromatic compounds, such as alkyl-substituted benzenes or naphthalenes wherein the alkyl groups attached to the aromatic ring contain at least about 8 carbon atoms, the wax-substituted benzenes and naphthalenes being particularly preferred. The petroleum sulfonic acids, also known as "sour oils," are those obtained in the treatment of petroleum oils, particularly refined, or semi-refined oils, with concentrated or fuming sulfuric acid, and which remain in the oil after settling out of sludge. These sulfonic acids may be represented by the general formula



where R is one or more alkyl, alkaryl or aralkyl groups and the aromatic nucleus is a single or condensed ring or partially hydrogenated ring.

The petroleum sulfonic acids employed in the process of the instant invention were sour oil treatments identified as A, B and C in Table II below and were prepared by sulfonation of a refined East Texas stock whose properties are listed below in Table I. The main points of difference between the prepared sulfonic acid materials A, B and C can be traced to the variations in acid-addition time, length of air blowing, and the settling time after air blowing.

TABLE I

Properties:	East Texas stock
K.V. @ 100° F., cs.	134.4
K.V. @ 210° F., cs.	12.22
Viscosity index	85
Sulfur, percent	0.23
Specific gravity	0.8922
A.P.I. gravity	27.1
Pour, ° F.	20
Flash, ° F.	490
Fire, ° F.	530
Color, Lovibond	42
Color, A.S.T.M.	7
Viscosity gravity constant @ 210° F.	0.822

The organic sulfonic acid product identified as Product A in Table II below was prepared in the following manner:

Thirty percent, by weight, of 103 to 104% sulfuric acid was added over a period of 41 minutes to air agitated charge oil (of the type identified in Table I) with the reaction mixture being maintained at 79 to 118° F.

Quench water (6%, by weight, of charge oil) was then added over a one-half hour period at 114 to 143° F., followed by 19.5 hour settling period at 143 to 163° F. The sludge and spent acid were withdrawn and the product blown with air for two hours at 138 to 157° F. A final settling period of 67.2 hours at 157 to 160° F. was carried out to insure as complete a removal as possible of spent acid and sludge. The final product had a total neutralization number of 29.9 and a true neutralization number of 22.9 and is further identified as Product A in Table II below. The additional sulfonated Products B and C, also indicated below in Table II, were prepared in a manner similar to that outlined above, the differing neutralization numbers resulting from a variation in the periods of acid treatment, air-blowing, etc.

TABLE II

Inspections	A	B	C
Total N.N.	29.9	37.2	30.0
True N.N.	22.0	31.9	25.0

In the following examples, procedures for the preparation of complex calcium sulfonate salts of the character contemplated by this invention are given in order to illustrate various aspects and modifications of the invention. The amounts of reagents, i.e., calcium hydroxide, barium hydroxide, formaldehyde, etc., as utilized, are based on the "total" acidity of the sour oil, which, as aforesaid, includes minor amounts of free sulfuric acid present therein. Calculations on the amount of metal incorporated into the final product were based on the "true" acidity, a measure of the organic acids present in the sour oil and are expressed in terms of the percentage excess metal over the actual amount of metal found in the corresponding normal salts.

Example 1

Materials:

(1) 300 g. sour oil A
(2) 18.6 g. lime (Greasemakers, 96%, 3.0 equivalents based upon total acidity), 56 ml. distilled water
(3) 53.5 g. 36% formaldehyde solution (4.0 equivalents based upon total acidity)

Procedure:

The lime-water slurry (2) was placed into a 1-liter, four-necked round bottom flask equipped with a mechanical stirrer, thermometer, air inlet tube, reflux condenser and dropping funnel. This slurry was heated to 75° C. and the sour oil (1) was added during a one-hour period. The resulting mixture was digested for an additional 30-minute period at a temperature of 75 to 80° C. To this mixture was added the formaldehyde solution (3) dropwise over a 30-minute period at 75 to 80° C. Maintaining the same temperature the product was digested for 30 minutes. Dehydration was effected by heating the reaction mixture to 115° C. while removing water with a Dean-Stark "take-off." To insure complete dehydration, the temperature was maintained at 110 to 115° C. for 30 minutes.

Twelve grams of "Hyflow" (a diatomaceous earth filter aid) were added with stirring and the product filtered through an electrically heated Buchner funnel (#1 Whatman filter paper) precoated with 6 grams of "Hyflow" to yield a bright, brownish-red oil.

Analysis of product:

Percent calcium=1.70 (124% in excess of normal salt)
Potentiometric Base No.=26.1

Example 2

Materials:

(1) 300 g. sour oil A
(2) 8.0 g. lime (Greasemakers, 96%, 1.3 equivalents based upon the total acidity)
50 g. distilled water

Complexing reagent:

(3) 12.4 g. lime (Greasemakers, 96%, 2.0 equivalents based upon the total acidity)
55 g. formaldehyde solution (36%, 4.12 equivalents based upon the total N.N.)
100 ml. distilled water

Procedure:

The petroleum sulfonic acid (1) was added to the aqueous slurry of lime (2) which was contained in a 1-liter, four-neck flask equipped with a mechanical stirrer, thermometer, air inlet tube, reflux condenser and a dropping funnel. Following this addition, which was carried out at 60 to 70° C. over a one-hour period, the mixture was digested for 30 minutes at 70 to 75° C. The complexing reagent was prepared in a separate flask (four-neck, round bottom, equipped in the same manner as the flask used to prepare the calcium sulfonate) by adding about 25% of the formaldehyde solution to the water lime slurry and heating. When the temperature reached 75 to 85° C. an exothermic, color-producing reaction occurred. The heat was removed and the reaction temperature was maintained by dropwise addition of the remaining portion of the formaldehyde solution. The product, a brown colored suspension, was stirred for 20 minutes (after cooling to 50° C.) to assure completeness of reaction. The calcium sulfonate was added dropwise to this reagent at 70 to 75° C. over a one-hour period. When the addition was complete, more heat was applied and the water was removed by means of a Dean-Stark "take-of." Following dehydration the mixture was maintained at 110 to 115° C. for one-half hour to insure dryness.

Twelve grams of "Hyflo" filter-aid were stirred into the product and 6 grams of "Hyflo" packed on top of the filter paper in an electrically heated Buchner funnel. Filtration yielded a brownish-red oil.

Analysis of product:

Percent calcium=2.22 (192% in excess of the normal salt)
Percent sulfur=1.44
Potentiometric Base No.=22.0
Kinematic Viscosity at 210° F., cs.=105.4

Example 3

Materials:

(1) 300 g. sour oil A
(2) 8.0 g. lime (Greasemakers, 96%, 1.3 equivalents based upon total acidity)
50 ml. distilled water

Complexing reagent:

(3*a*) 18.6 g. lime (Greasemakers, 96%, 3.0 equivalents based upon total acidity)
100 ml. distilled water
(3*b*) 53.3 g. formaldehyde (36% solution 4.0 equivalents based upon total acidity)

Procedure:

The petroleum sulfonic acid (1) was added to the aqueous slurry of lime (2) which was contained in a one-liter, four-neck flask equipped with a mechanical stirrer, thermometer, air inlet tube, dropping funnel and reflux condenser. Following this addition which was carried out at 70° C. over a one-hour period the mixture was digested for one hour at 90 to 100° C. The complexing reagent was prepared in a separate flask by adding the formaldehyde solution (3*b*) dropwise to the lime slurry (3*a*) at 50° C. and digested one hour at this temperature. This reagent was then added to the calcium sulfonate at 70° C. over a 45-minute period. When the addition was com-

plete, more heat was applied and the water removed by means of a Dean-Stark "take-off." Following the dehydration the mixture was maintained at 110 to 115° C. for one hour to insure dryness.

Twelve grams of "Hyflo" filter-aid were stirred into the product and 6 grams of "Hyflo" packed on top of the filter paper in an electrically heated Buchner funnel and the mixture filtered.

Analysis of product:
- Percent calcium=2.06 (173% in excess of the normal salt)
- Potentiometric Base No.=(strong) 5.3, (total) 29.0
- Kinematic Viscosity at 210° F., cs.=38.61
- Percent sulfur=1.36

Example 4

Materials:
- (1) 300 g. sour oil A
- (2) 11.2 g. lime (Greasemakers, 96%, 1.8 equivalents based upon total acidity)
- 50 ml. distilled water

Complexing reagent:
- (3) 15.5 g. lime (Greasemakers, 96%, 2.5 equivalents based upon the total acidity)
- 26.7 g. formaldehyde solution (36%, 2.0 equivlents based upon the total acidity)

Procedure:

The sour oil (1) was added to the aqueous slurry of lime (2) which was contained in a one-liter, four-neck flask equipped with a mechanical stirrer, thermometer, air inlet tube and reflux condenser. Following this addition, which was carried out at 70 to 75° C. over an hour, the mixture was digested for an additional hour at 70 to 75° C. The complexing reagent was formed in a separate flask equipped with a reflux condenser, mechanical stirrer, and dropping funnel, by reacting about 25% of the formaldehyde solution with the lime water slurry at 60 to 70° C. Once the exothermic, color forming reaction had started the rest of the formaldehyde solution was added slowly keeping the mixture below reflux temperature. This product (3) was stirred for one hour to assure completeness of reaction and was then added dropwise to the calcium sulfonate at 70 to 75° C. over a one-hour period. When the addition was complete, a Dean-Stark "take-off" was included in the system and more heat was applied. Following the dehydration to 120 to 125° C. the mixture was maintained at this same temperature for one hour to assure dryness.

Twelve grams of "Hyflo" filter-aid were stirred into the product and the mixture filtered through an electrically heated Buchner funnel (packed with 6 g. "Hyflo") yielding a clear, reddish-brown oil.

Analysis of product:
- Percent calcium=1.96 (158% in excess of normal salt)
- Potentiometric Base No.=7.3 (strong), 30 (total)
- Kinematic Viscosity at 210° F., cs.=36.07
- Percent sulfur=1.39

Example 5

Materials:
- (1) 300 g. sour oil C
- (2) 9.3 g. lime (Greasemakers, 96%, 1.5 equivalents based upon the total acidity)
- 21.0 g. distilled water

Complexing reagent:
- (3) 38.6 g. 36% formaldehyde solution (2.88 equivalents based upon total acidity)
- (4) 12.4 g. lime (Greasemakers, 96%, 2.0 equivalents based upon total acidity)
- 25.0 ml. distilled water

Procedure:

The petroleum sulfonic acid (1) was added to the aqueous slurry of lime (2) which was contained in a one-liter, four-neck flask equipped with a mechanical stirrer, thermometer, air inlet tube, reflux condenser and a dropping funnel. Following this addition, which was carried out at 60 to 70° C. over ¾-hour period, the mixture was digested one hour at reflux. The reaction was cooled to 90° C. and the formaldehyde solution (3) was added dropwise, followed by the lime water slurry (4) and the mixture was further digested. A Dean-Stark "take-off" was introduced into the system and the heat increased to remove the water. Following dehydration to 110 to 115° C. The mixture was maintained at 110 to 115° C. for one hour to insure dryness.

Twelve grams of "Hyflo" filter-aid were added and the mixture filtered through an electrically heated Buchner funnel (#1 Whatman filter paper) precoated with 6 grams of "Hyflo" to yield a brownish oil.

Analysis of product:
- Percent calcium=2.00 (160% in excess of normal salt)
- Potentiometric Base No.=(strong) 5.4, (total) 32.0
- Kinematic Viscosity at 210° F., cs.=44.22

Example 6

Materials:
- (1) 300 g. sour oil B
- (2) 6.4 g. $Mg(OH)_2$ (1.1 equivalents based upon the total acidity)
- 50 ml. distilled water

Complexing reagent:
- (3) 11.55 g. $Mg(OH)_2$ (2.0 equivalents based upon the total acidity)
- 33.2 g. 36% formaldehyde solution (2.0 equivalents based upon the total acidity)
- 100 ml. distilled water

Procedure:

The procedure was essentially the same as Example 4 with the exception that no color change was noted in the preparation of the complexing reagent.

Analysis of product:
- Magnesium, percent=1.32 (162% excess over the theoretical normal salt[1]
- Percent sulfur=1.93
- Potentiometric Base No.=6.7
- Kinematic Viscosity at 210° F., cs.=48.44

[1] Calculated from percent Mg equivalent to the calcium normal salt.

Example 7

Materials:
- (1) 300 g. sour oil B
- (2) 14.4 g. potassium hydroxide (85% KOH by assay, 1.1 equivalents based upon the total acidity)
- (3) 50 ml. distilled water

Complexing reagent:
- (4) 26.2 g. potassium hydroxide (2.0 equivalents based upon total acidity)
- 33.2 g. 36% formaldehyde solution (2.0 equivalents based upon total acidity)
- 100 ml. distilled water

Procedure:

The preparative methods used were the same as disclosed in Example 4.

Analysis of product:
- Percent potassium=4.17 (158% excess over the theoretical normal salt[2])
- Potentiometric Base No.=35
- Percent sulfur=1.49
- Kinematic Viscosity at 210° F., cs.=47.18

[2] Calculated from percent potassium equivalent to the calcium normal salt.

Example 8

Materials:

(1) 300 g. sour oil B

(2) 31.4 barium hydroxide octahydrate (1.0 equivalent based upon the total acidity)
50 ml. distilled water

Complexing reagent:

(3) 33.0 g. 36% formaldehyde solution (2.0 equivalents based upon the total acidity)
57.2 g. barium hydroxide octahydrate (1.82 equivalents based upon the total acidity)
100 ml. distilled water

Procedure:

The same procedure was employed as described in Example 4.

Analysis of product:

Percent barium=6.70 (130% excess over theoretical normal salt[3])
Potentiometric Base No.=15
Percent sulfur=1.50
Kinematic Viscosity at 210° F., cs.=29.23

[3] Calculated from percent barium equivalent to the calcium normal salt.

Example 9

Materials:

(1) 300 g. sour oil B

(2) 9.0 sodium hydroxide (1.1 equivalents based upon the total acidity)
50 ml. distilled water

Complexing reagent:

(3) 16.5 g. sodium hydroxide (2.0 equivalents based upon the total acidity)
33.2 g. formaldehyde solution (2.0 equivalents based upon the total acidity)
100 ml. distilled water

Procedure:

The procedure was essentially the same as described in Example 4.

Analysis of product:

Percent sodium=1.97 (105% excess over theoretical normal salt[4])
Potentiometric Base No.=27
Percent sulfur=1.53
Kinematic Viscosity at 210° F., cs.=48.15

[4] Calculated from percent sodium equivalent to the calcium normal salt.

PREPARATION OF WAX-BENZENE (2–12) SULFONIC ACID

A paraffin wax having an average of 24 carbon atoms per molecule and a melting point of 126° F. was chlorinated at a temperature of about 100° C. with chlorine gas until the weight of the wax had increased about 12%. The chlorowax thus obtained was then blown with nitrogen to remove any occulded chlorine and hydrogen chloride.

A 1000-gram portion of the chlorowax was then mixed with 500 grams of benzene in a 3-necked flask equipped with a stirrer, reflux condenser and a thermometer. The mixture was heated to a temperature of 60° C. Aluminum chloride was then added slowly over a period of two hours. The addition of aluminum chloride was accompanied by a vigorous evolution of hydrogen chloride. The temperature was then raised to a temperature of 80° C. and held there for one hour. The excess benzene was then removed by inverting the reflux condenser and heating to a temperature of 116° C. Two hundred milliliters of benzene were thus recovered. The mixture was cooled to a temperature of 60° C. and then another 1000 grams of chlorowax were added slowly. After completing the addition of this chlorowax, the temperature was raised to 100° C. and held there for one hour. The product was allowed to stand overnight at a temperature of about 60° C., and then was separated from the sludge by decantation and filtered by suction through clay.

Seventeen hundred and thirty-eight grams of wax-benzene thus obtained were placed in a 3-necked flask equipped with a stirrer and a thermometer and heated to a temperature of 40° C. Eight hundred and sixty-nine grams of oleum (15% SO_3) were added slowly to the wax-benzene from a dropping funnel at a rate regulated to maintain the temperature below 50° C. The addition of oleum consumed about 3 hours. The mixture was then stirred for an additional hour to ensure complete reaction. The mixture was then poured into 1000 milliliters of water and subsequently 1810 grams of mineral oil were added to the mixture. The mixture thus obtained was stirred thoroughly and then allowed to stand until the water separated into a layer. The water layer was then drained off. The product thus obtained was approximately a 50% blend of wax-benzene sulfonic acid in mineral oil and had a neutralization number of 41.

It will be understood that a wax-benzene prepared according to the foregoing procedure in which a quantity of chlorowax containing 2 atomic proportions of chlorine and having a chlorine content of 12% is reacted with 1 mol of benzene is designated "wax-benzene (2–12)." Similarly, "wax-benzene (3–10)" and "wax-benzene (1–10)" may also be prepared by the reaction of sufficient amounts of chlorinated wax, containing 10%, by weight, of chlorine, to provide 3 atomic proportions and 1 atomic proportion of chlorine per mol of benzene, respectively, in the reaction and are useful in the invention. In general, the amount of chlorowax containing from about 10 to about 18%, by weight, of chlorine used in the reaction is sufficient to supply between 1 and 4 atomic proportions of chlorine per mol of benzene used.

Example 10

Materials:

(1) 200 g. wax-benzene (2–12) sulfonic acid (total N.N.=41, true N.N.=41—see above)
100 g. mineral oil (SUV of 100 sec. at 100° F., acid-refined Mid-Continent)
7.2 g. lime (Greasemakers, 96%, 1.3 equivalents on total acidity)
50 ml. distilled water

Complexing reagent:

(2) 11.2 g. lime (2.0 equivalents on total acidity)
48.8 g. 36% formaldehyde solution (4.0 equivalents on total acidity)
75 ml. distilled water

Procedure:

The wax-benzene sulfonic acid, oil, lime and water were placed in a 1-liter, four-neck flask equipped with a mechanical stirrer, Dean-Stark "take-off," reflux condenser, nitrogen inlet tube and thermometer. The mixture was heated to 55° C.±5° C. and held at this temperature for one hour. The complexing reagent (2) was prepared by the same procedure as outlined in Example 3. This was added to the calcium sulfonate (1) over a 5 to 6-minute period at 50 to 60° C. The heat was increased and the water was removed by means of a Dean-Stark "take-off." When a temperature of 150° C. had been reached the mixture was maintained at this temperature for 30 minutes. The product was cooled to 110 to 115° C. and treated with 15 grams of "Hyflo" filter-aid and then filtered through an electrically heated Buchner funnel packed with 5 grams of "Hyflo" yielding a brownish-red oil.

Analysis of product:

Percent calcium=1.87 (117% in excess of normal salt)

Example 11

Materials:

(1) 400 g. sour oil C

(2) 13.2 g. lime (Greasemakers, 96%, 1.3 equivalents based upon the total acidity)
53 ml. water distilled

Complexing reagent:

(3) 17.6 g. lime (Greasemakers, 96%, 2.0 equivalents based upon the total acidity)
18.8 g. paraformaldehyde (2.96 equivalents, as formaldehyde, based upon the total N.N.)
100 g. distilled water

Procedure:

The petroleum sulfonic acid (1) was added to the aqueous slurry of lime (2) which was contained in a one-liter, four-neck flask equipped with a mechanical stirrer, thermometer, air inlet tube and reflux condenser. Following this addition, which was carried out at 70 to 75° C. over a one-hour period, the mixture was digested for an additional hour at 70 to 75° C. The complexing reagent was formed in a separate flask equipped with reflux condenser, mechanical stirrer and a dropping funnel by reacting about 25% of the paraformaldehyde (in slurry) with the lime-water slurry at 60 to 70° C. Once the exothermic, color-producing reaction had started the rest of the paraformaldehyde slurry was added slowly. The product (3) was stirred for one hour to assure complete reaction and was then added dropwise to the calcium sulfonate at 70 to 75° C. over a one-hour period. When addition was complete a Dean-Stark "take-off" was included in the system and more heat was applied. Following the dehydration to 120 to 125° C., the mixture was maintained at 110 to 120° C. for one hour to insure dryness. Sixteen grams of "Hyflo" filter-aid were stirred into the product and the mixture filtered through an electrically heated Buchner funnel, packed with 8 grams of "Hyflo," yielding 382 grams of a reddish-brown oil.

Analysis of product:

Percent calcium=1.95 (153% in excess of the normal salt)
Potentiometric Base No.=5.9
Kinematic Viscosity at 210° F., cs.=69.90
Percent sulfur=1.43

Example 12

Materials:

(1) 800 g. sour oil B

(2) 307. g. lime (Greasemakers, 96%, 1.5 equivalents based upon the total acidity)
150 ml. distilled water

Complexing reagent:

(3) 88.9 g. formaldehyde (36% solution, 2.0 equivalents based upon the total acidity)

(4) 41.0 g. lime (Greasemakers, 96%, 2.0 equivalents based upon the total acidity)
400 ml. distilled water

Procedure:

Except for the size of reaction vessels, the procedure was the same as in Example 4.

Analysis of product:

Percent calcium=1.93 (130% excess metal)
Potentiometric Base No.=(strong) 3.2, (total) 30

ENGINE EVALUATION

To demonstrate the ability of the complex formaldehyde-sulfonate metal salts of the invention as oil detergents, a series of oil blends thereof were prepared and tested in the Lauson D–42 engine detergency test and in the CFR diesel D–21 detergency test. The base oil used in these tests contained 1.0% of an antioxidant (Pinene-P_2S_5 reaction product). The results are given in Tables III and IV.

LAUSON D–4A DETERGENCY TEST

This test determines the effectiveness of the lubricating oil in preventing fouling as measured by the cleanliness of rings, lands, ring grooves and piston skirts. Cleanliness ratings are based on a scale of from 100 to 0, a 100 rating signifying a perfectly clean condition and a 0 rating representing the worst possible deposit condition. Bearing weight loss is also measured as supplemental data.

A single cylinder, 4-cycle, liquid cooled Lauson engine with splash lubrication and having copper-lead bearings is used. The operating conditions are as follows:

Oil temperature	225° F.
Jacket temperature	275° F.
Speed	1825 r.p.m.
Brake load	1.6 H.P.

One-half throttle.
13–1 air-fuel ratio.
Oil added every 20 hours (one-gallon sample used).

The engine is inspected at the end of 20, 60 and 100 hours, the duration of the test being 100 hours. The fuel used is a controlled "Mobilgas Special" type blend gasoline (40% thermal +30% catalytically cracked +30% straight run +25 cc. TEL/gal.).

DIESEL (D–21) DETERGENCY TEST

This test determines the effectiveness of the lubricating oil in preventing piston deposits and top ring wear.

A single cylinder C.F.R., 4-cycle, super-charged, diesel engine is used. The operating conditions are as follows:

Oil temperature	175° F.
Jacket temperature	212° F.
Speed	1800 r.p.m.
Brake load	7.5 H.P.

Oil addition every 8 hours starting at 4 hours (1½ gal. sample used).

Heat input	1260 B.t.u./min.

The duration of the test is 60 hours. The fuel used is a No. 2 fuel oil containing 1% sulfur. The results are reported in terms of piston cleanliness ratings as in the D–4 test.

The amount of complex salt product utilized in a lubricating oil will depend upon the particular oil and the application for which it is designed. Generally, amounts ranging from about 0.1 up to about 40 weight percent may be used, the usual amount being from about 0.5 to about 10 weight percent.

The complex salt products of this invention may be used in lubricating oil compositions containing other addition agents designed to improve the oil in different respects, e.g., anti-oxidants, extreme pressure agents, pour point depressants, viscosity index improvers, defoamants, etc.

Although the complex salts of this invention are intended primarily for use as lubricating oil additives, they are also adaptable for use in other applications, e.g., they find application in the manufacture of detergent soaps and are useful as dispersants and rust preventives. They may also be used as additives for cutting and textile oils.

Although the proportions and utility of certain specific representative complex salt products and oil compositions thereof have been described in detail herein, it is not intended that the invention be limited in any way thereby, but that it include such variations and procedures and such products and compositions as come within the spirit and scope of the accompanying claims.

TABLE III.—C.F.R. DIESEL (D-21) TEST ON METAL HYDROXIDE-FORMALDEHYDE COMPLEX SULFONATES

Example number	Reagents [1] equivalents of metal hydroxide		Metal hydroxide used	Mols formaldehyde [2]	Percent metal found	Percent metal [3] excess	Percent detergent	Percent metal in oil	Base oil plus 1.0% antioxidant,[4] cleanliness rating at 60 hours
	Normal salt	Complexing reagent							
	Base oil [5] alone								67
	Base oil plus 1.0% antioxidant								62
1	3.0		$Ca(OH)_2$	4.0	1.70	124	3.4	0.058	84
2	1.3	2.0	$Ca(OH)_2$	4.12	2.22	192	4.0	0.088	84
3	1.3	3.0	$Ca(OH)_2$	4.0	2.06	173	4.3	0.088	89
4	1.8	2.5	$Ca(OH)_2$	2.0	1.96	158	4.5	0.088	88
5	1.5	2.0	$Ca(OH)_2$	2.88	2.00	160	4.4	0.088	85
6	1.1	2.0	$Mg(OH)_2$	2.0	1.32	[6] 162	3.85	0.050	83
7	1.1	2.0	KOH	2.0	4.17	[6] 158	2.1	0.088	84
8	1.0	1.82	$Ba(OH)_2.8H_2O$	2.0	6.70	[6] 130	3.0	0.20	83
9	1.1	2.0	NaOH	2.0	1.97	[6] 105	5.16	0.10	83
10 [7]	1.3	2.0	$Ca(OH)_2$	4.0	1.87	117	4.7	0.088	87
11	1.3	2.0	$Ca(OH)_2$	[8] 2.93	1.95	153	4.5	0.088	87

[1] Per equivalent of sulfonic acid, based upon the total N.N.
[2] Expressed as mols per equivalent of sulfonic acid.
[3] Based on actual values found in normal salt.
[4] Pinene, P_2S_5 reaction product.
[5] SAE 30 grace solvent refined Mid-Continent oil (K.V. at 100° F.=121; K.V. at 210° F.=12.2).
[6] Calculated from normal salt equivalent to the calcium normal salt.
[7] Wax-Benzene (2-12) sulfonic acid used in place of the petroleum sulfonic acid.
[8] Paraformaldehyde substituted for formaldehyde solution.

TABLE IV.—LAUSON D4-A TEST ON CALCIUM HYDROXIDE-FORMALDEHYDE-COMPLEX SULFONATES

Example number	Reagents [1] Equivalents of $Ca(OH)_2$		Mols [4] of HCHO	Percent Calcium	Percent Calcium Excess [5]	Lauson D4-A Test Base Oil [2] Plus 1.0% Antioxidant [3]		
	Normal Salt	Complexing Reagent				Percent Detergent	Percent Calcium in Oil	Cleanliness Rating at 100 Hours
	Base oil alone							58
	Base oil + 1.0% antioxidant							59
12	1.5	2.0	2.0	1.93	130	4.56	0.088	79

[1] Per equivalent sulfonic acid, based on total N.N.
[2] RN 183-B: SAE 20 grade solvent-refined Pennsylvania oil (K.V. at 100° F.=63; K.V. at 210° F.=8.3).
[3] Pinene-P_2S_5 reaction product.
[4] Expressed as mols per equivalent of sulfonic acid.
[5] Based on actual amount found in normal salt.

What is claimed is:

1. A method for preparing a complex metal salt of a sulfonic acid selected from the group consisting of oil-soluble petroleum sulfonic acids and oil-soluble alkaryl sulfonic acids, said complex metal salt containing from 105% to about 192% excess metal over that corresponding to a normal metal salt of said acid, said method comprising the steps of (1) intimately contacting a hydrocarbon solution of the sulfonic acid in the presence of water with the hydroxide of a metal selected from Groups I and II of Mendeleeff's Periodic Table of the Elements in an amount to supply at least about one equivalent of metal per equivalent of acid-hydrogen content in said sulfonic acid solution, at a temperature of from about 25° C. to about 100° C., (2) intimately contacting the reaction mixture formed in step 1 in the presence of water with formaldehyde and the hydroxide of a metal selected from Groups I and II of Mendeleeff's Periodic Table of the Elements at a temperature of from 25° C. to about 100° C., the amount of formaldehyde being from about 2 to about 4 equivalents per equivalent of sulfonic acid in said sulfonic acid solution, and the amount of metal hydroxide present in said reaction mixture along with said formaldehyde being that sufficient to supply at least about two equivalents of metal per equivalent of acid-hydrogen content in said sulfonic acid solution, (3) substantially completely dehydrating the reaction mixture from step 2 and (4) filtering off insoluble materials from said reaction mixture.

2. A method for preparing metal a complex salt of an oil-soluble petroleum sulfonic acid, said complex metal salt containing from 105% to about 192% excess metal over that corresponding to a normal metal salt of said acid, said method comprising the steps of (1) intimately contacting a hydrocarbon solution of the sulfonic acid in the presence of water with the hydroxide of a metal selected from Groups I and II of Mendeleeff's Periodic Table of the Elements in an amount to supply at least about one equivalent of metal per equivalent of acid-hydrogen content in said sulfonic acid solution, at a temperature of from about 25° C. to about 100° C., (2) intimately contacting the reaction mixture formed in step 1 in the presence of water with formaldehyde and the hydroxide of a metal selected from Groups I and II of Mendeleeff's Periodic Table of the Elements at a temperature of from 25° C. to about 100° C., the amount of formaldehyde being from about 2 to about 4 equivalents per equivalent of sulfonic acid in said sulfonic acid solution, and the amount of metal hydroxide present in said reaction mixture along with said formaldehyde being that sufficient to supply at least about two equivalents of metal per equivalent of acid-hydrogen content in said sulfonic acid solution, (3) substantially completely dehydrating the reaction mixture from step 2 and (4) filtering off insoluble materials from said reaction mixture.

3. A method for preparing a complex metal salt of an oil-soluble petroleum sulfonic acid, said complex metal salt containing from 105% to about 192% excess metal over that corresponding to a normal metal salt of said acid, said method comprising the steps of (1) intimately contacting an oil solution of the sulfonic acid in the presence of water with calcium hydroxide in an amount to supply at least about one equivalent of metal per equivalent of acid-hydrogen content in said sulfonic acid solution, at a temperature of from about 25° C. to about 100° C., (2) intimately contacting the reaction mixture

formed in step 1 in the presence of water with formaldehyde and calcium hydroxide at a temperature of from 25° C. to about 100° C., the amount of formaldehyde being from about 2 to about 4 equivalents per equivalent of sulfonic acid in said sulfonic acid solution, and the amount of calcium hydroxide present in said reaction mixture along with said formaldehyde being that sufficient to supply at least about two equivalents of calcium per equivalent of acid-hydrogen content in said sulfonic acid solution, (3) substantially completely dehydrating the reaction mixture from step 2 and (4) filtering off insoluble materials from said reaction mixture.

4. A method for preparing a complex metal salt of an oil-soluble petroleum sulfonic acid, said complex metal salt containing from 105% to about 192% excess metal over that corresponding to a normal metal salt of said acid, said method comprising the steps of (1) intimately contacting an oil solution of the sulfonic acid in the presence of water with barium hydroxide in an amount to supply at least about one equivalent of metal per equivalent of acid-hydrogen content in said sulfonic acid solution, at a temperature of from about 25° C. to about 100° C., (2) intimately contacting the reaction mixture formed in step 1 in the presence of water with formaldehyde and barium hydroxide at a temperature of from 25° C. to about 100° C., the amount of formaldehyde being from about 2 to about 4 equivalents per equivalent of sulfonic acid in said sulfonic acid solution, and the amount of barium hydroxide present in said reaction mixture along with said formaldehyde being that sufficient to supply at least about two equivalents of barium per equivalent of acid-hydrogen content in said sulfonic acid solution, (3) substantially completely dehydrating the reaction mixture from step 2 and (4) filtering off insoluble materials from said reaction mixture.

5. A method for preparing a complex metal salt of an oil-soluble petroleum sulfonic acid, said complex metal salt containing from 105% to about 192% excess metal over that corresponding to a normal metal salt of said acid, said method comprising the steps of (1) intimately contacting an oil solution of the sulfonic acid in the presence of water with potassium hydroxide in an amount to supply at least about one equivalent of metal per equivalent of acid-hydrogen content in said sulfonic acid solution, at a temperature of from about 25° C. to about 100° C., (2) intimately contacting the reaction mixture formed in step 1 in the presence of water with formaldehyde and potassium hydroxide at a temperature of from 25° C. to about 100° C., the amount of formaldehyde being from about 2 to about 4 equivalents per equivalent of sulfonic acid in said sulfonic acid solution, and the amount of potassium hydroxide present in said reaction mixture along with said formaldehyde being that sufficient to supply at least about two equivalents of potassium per equivalent of acid-hydrogen content in said sulfonic acid solution, (3) substantially completely dehydrating the reaction mixture from step 2 and (4) filtering off insoluble materials from said reaction mixture.

6. A method for preparing a complex metal salt of an oil-soluble alkyl aryl sulfonic acid, said complex metal salt containing from 105% to about 192% excess metal over that corresponding to a normal metal salt of said acid, said method comprising the steps of (1) intimately contacting an oil solution of the alkyl aryl sulfonic acid, in the presence of water, with the hydroxide of a metal selected from Groups I and II of Mendeleeff's Periodic Table of the Elements in an amount to supply at least about one equivalent of metal per equivalent of acid-hydrogen content in said sulfonic acid solution, at a temperature of from about 25° C. to about 100° C., (2) intimately contacting the reaction mixture formed in step 1 in the presence of water with formaldehyde and the hydroxide of a metal selected from Groups I and II of Mendeleeff's Periodic Table of the Elements at a temperature of from 25° C. to about 100° C., the amount of formaldehyde being from about 2 to 4 equivalents per equivalent of sulfonic acid in said sulfonic acid solution, and the amount of metal hydroxide present in said reaction mixture along with said formaldehyde being that sufficient to supply at least about two equivalents of metal per equivalent of acid-hydrogen content in said sulfonic acid solution, (3) substantially completely dehydrating the reaction mixture from step 2 and (4) filtering off insoluble materials from said reaction mixture.

7. A method for preparing a complex metal salt of an oil-soluble wax-benzene sulfonic acid, said complex metal salt containing from 105% to about 192% excess metal over that corresponding to a normal metal salt of said acid, said method comprising the steps of (1) intimately contacting a hydrocarbon solution of the wax-benzene sulfonic acid in the presence of water with calcium hydroxide in an amount to supply at least about one equivalent of calcium per equivalent of acid-hydrogen content in said sulfonic acid solution, at a temperature of from about 25° C. to about 100° C., (2) intimately contacting the reaction mixture formed in step 1 in the presence of water with formaldehyde and calcium hydroxide, at a temperature of from 25° C. to about 100° C., the amount of formaldehyde being from about 2 to about 4 equivalents per equivalent of sulfonic acid in said sulfonic acid solution, and the amount of calcium hydroxide present in said reaction mixture along with said formaldehyde being that sufficient to supply at least about two equivalents of calcium per equivalent of acid-hydrogen content in said sulfonic acid solution, (3) substantially completely dehydrating the reaction mixture from step 2 and (4) filtering off insoluble materials from said reaction mixture.

8. A method for preparing a complex metal salt of an oil-soluble wax-benzene sulfonic acid, said complex metal salt containing from 105% to about 192% excess metal over that corresponding to a normal metal salt of said acid, said method comprising the steps of (1) intimately contacting a hydrocarbon solution of the wax-benzene sulfonic acid in the presence of water with barium hydroxide in an amount to supply at least about one equivalent of barium per equivalent of acid-hydrogen content in said sulfonic acid solution at a temperature of from about 25° C. to about 100° C., (2) intimately contacting the reaction mixture formed in step 1 in the presence of water with formaldehyde and barium hydroxide, at a temperature of from 25° C. to about 100° C., the amount of formaldehyde being from about 2 to about 4 equivalents per equivalent of sulfonic acid in said sulfonic acid solution, and the amount of barium hydroxide present in said reaction mixture along with said formaldehyde being that sufficient to supply at least about two equivalents of barium per equivalent of acid-hydrogen content in said sulfonic acid solution, (3) substantially completely dehydrating the reaction mixture from step 2 and (4) filtering off insoluble materials from said reaction mixture.

9. A method for preparing a complex metal salt of an oil-soluble wax-benzene sulfonic acid, said complex metal salt containing from 105% to about 192% excess metal over that corresponding to a normal metal salt of said acid, said method comprising the steps of (1) intimately contacting a hydrocarbon solution of the wax-benzene sulfonic acid in the presence of water with potassium hydroxide in an amount to supply at least about one equivalent of potassium per equivalent of acid-hydrogen content in said sulfonic acid solution at a temperature of from about 25° C. to about 100° C., (2) intimately contacting the reaction mixture formed in step 1 in the presence of water with formaldehyde and potassium hydroxide, at a temperature of from 25° C. to about 100° C., the amount of formaldehyde being from about 2 to 4 equivalents per equivalent of sulfonic acid in said sulfonic acid solution, and the amount of potassium hydroxide

present in said reaction mixture along with said formaldehyde being that sufficient to supply at least about two equivalents of potassium per equivalent of acid-hydrogen content in said sulfonic acid solution, (3) substantially completely dehydrating the reaction mixture from step 2 and (4) filtering off insoluble materials from said reaction mixture.

10. The method of preparing a highly basic lubricating oil concentrate comprising: adding to an oil-soluble alkaline earth metal sulfonate dissolved in mineral oil, an alkaline earth metal hydroxide in an amount to provide up to 2.5 moles of said hydroxide per mole of sulfonate, formaldehyde in an amount sufficient to provide 2–4 moles of formaldehyde per mole of hydroxide and water at a temperature of about 60–100° C., removing the volatile components by heating and filtering the resulting product.

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DANIEL E. WYMAN, *Primary Examiner.*

LEON ZITVER, JULIUS GREENWALD, *Examiners.*

R. W. HABEL, B. M. EISEN, R. E. HUTZ, P. P. GARVIN, *Assistant Examiners.*