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3,133,019

METHOD FOR PREPARING HIGH METAL-CONTENT SALTS OF SULFONIC ACIDS

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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 contents. Metal sulfonates, such as metal salts of petroleum sulfonic acids (obtained by the sulfonation of petroleum oils) and of synthetic sulfonic acids (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 200% to about 300% 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 the invention.

The process of this invention involves the reaction of a petroleum sulfonic acid or a synthetic alkyl aromatic

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sulfonic acid with a combination of reagents comprising a metal hydroxide, formaldehyde and acetic acid. The resulting products are oil-soluble complex metal sulfonates which possess high activity as motor oil detergents when added to conventional lubricating oil stocks.

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 1 equivalent of metal per equivalent of acid-hydrogen present in said sulfonic acid solution, (2) forming a reaction mixture comprising the reaction product from step 1 with formaldehyde, a metal hydroxide and acetic acid, in the presence of water, the amount of formaldehyde, metal hydroxide and acetic acid provided in said mixture being from about 2 to about 4 equivalents (mols) of formaldehyde, from about 1 to about 5 equivalents of metal hydroxide and from about 0.3 to about 1.0 equivalent of acetic acid per equivalent of acid-hydrogen present in the sulfonic acid solution employed in step 1, (3) substantially completely dehydrating the reaction mixture from step 2, and (4) filtering the resulting reaction mixture to remove insolubles therefrom.

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 solvent, preferably a petroleum 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 diluent oil for the purpose of the 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 reaction. 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-acetic acid mixture is prepared separately (by adding the acetic acid slowly to the formaldehyde) and then added slowly to the reaction mixture. When this last addition is completed, the reaction mixture is digested for a period of about thirty minutes to one hour. Dehydration of the reaction mixture is then effected by raising the temperature thereof to, say, 105° 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 from the

product, the oil solution thus obtained being directly blendable with lubricating oil to give a finished oil composition.

Although the aforesaid procedure is the one generally used, the manner and time of bringing the sulfonic acid solution and the complexing reagents together may be varied somewhat without markedly affecting the reaction or yield of complex salt product obtained. 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.

The new product formed in accordance with the present invention is different from the products described in the copending application of Ferdinand P. Otto, Serial No. 668,031, filed June 26, 1957, in that an extra reagent, the acetic acid, is used and metal contents of the complex salts obtained are greater than those of the products of that application. The new product is also different from the products described in U.S. Patent No. 2,739,125 in that the use of formaldehyde along with the acetic acid provides complex salts of greater metal contents than those provided by the process of the patent. Only the concurrent use of the formaldehyde and acetic acid will provide the high metal content products herein contemplated. Although it is not known exactly how the several reactants combine to form the complex salts of the present invention, the heterogeneity of the new product is greater than that of the previous complexes and it is believed that this greater heterogeneity makes possible the obtainment of the greater metal contents.

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-stage 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-acetic acid 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. Also, as indicated hereinabove, substantially complete dehydration is essential to the formation of these complex salts.

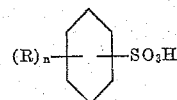
The metal hydroxides employed in the present invention are those of calcium, barium and magnesium, calcium hydroxide being particularly preferred. With respect to the amount of metal hydroxide reagent utilized in the process of the invention it will be appreciated that the formation of the high metal content complex salt requires (a) the reaction of the sulfonic acid (solution) with an amount of metal hydroxide at least sufficient to form a normal salt and (b) the reaction of the normal salt with a reagent formed from formaldehyde, acetic acid and metal hydroxide, i.e., a formaldehyde-acetic acid-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 the addition of formaldehyde and acetic acid (together or separately) to the initial metal hydroxide-sulfonic acid reaction mixture in which there is already present an excess of metal hydroxide, thereby forming the said complexing reagent in situ. On the other hand, where an excess of metal hydroxide (over that required to form the normal salt) was not used in the initial reaction mixture, additional metal hydroxide must be added along with the formaldehyde and acetic acid reagents. The total amount of the metal hydroxide employed in the process should preferably be at least about 3 equivalents, and

generally no more than 6 equivalents, per equivalent of acid-hydrogen in the sulfonic acid solution used, as the use of larger amounts tends to cause difficulty in filtration of the product, without providing a proportionate increase in the metal content of the complex salt product.

The amount of formaldehyde used may vary somewhat and is influenced by the amount of acetic acid or acetate employed. Preferably between 2 and 4 equivalents (mols) of formaldehyde per equivalent of acid-hydrogen in the sulfonic acid solution should be used.

The amount of acetic acid employed is relatively small. A lower limit of about 0.3 to 0.4 equivalent of acetic acid based on the acid-hydrogen content of the sulfonic acid solution is necessary to obtain significant improvement in metal content of the complex salt product over that obtained with formaldehyde alone, while an upper limit is subject to practical considerations in that filtration difficulties arise with the use of more than about 1.0 equivalent of the acid in the process.

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.

Typical "sour oil" sulfonic acids were prepared by sulfonation of a refined East Texas stock whose properties are listed below in Table I.

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
Spec. 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° F. to 118° F. Quench water (6%, by weight, of charge oil) was then added over a ½ hour period at 114° F. to 143° F., followed by 19.5 hour settling period at 143° F. to 163° F. The sludge and spent acid were withdrawn and the product blown with air for two hours at 138° F. to 157° F. A final settling period of 67.2 hours at 157° F. to 160° F. was carried out to insure as complete a removal as pos-

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sible of spent acid and sludge. The final product had a total neutralization number of 30 and a true neutralization number of 25 and is further identified as product A in Table II below.

The additional sulfonated products B and C, also indicated in Table II, were prepared in the manner outlined above, the differing neutralization numbers resulting from a variation in the periods of acid treatment, air-blowing, etc.

TABLE II

Inspections	Sour Oil A	Sour Oil B	Sour Oil C
Total N. N.-----	30	32	35
True N. N.-----	25	29	27

In the following examples, several procedures for the preparation of complex metal sulfonate salts of the character contemplated by this invention are presented. In these examples, the amounts of reagents, i.e., metal hydroxide, formaldehyde and acetic acid utilized (except where indicated otherwise) were 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 sulfonic acids present in the sour oil and are expressed in terms of the percentage excess metal over the actual amount of metal found in, or estimated for, the corresponding normal salts.

Example 1

Reactants:	Grams
(a) Sour oil A-----	400
(b) Lime, 96% (1.5 equivalents based on total N.N.)-----	12.2
(c) Water-----	28
(d) Lime, 96% (2.0 equivalents)-----	16.5
(e) Water-----	38
(f) Formaldehyde, 36% (2.4 equivalents)-----	43.0
(g) Acetic acid, glacial (0.3 equivalent)-----	3.86
(h) Water-----	20

Procedure.—A slurry of lime and water (b+c) was heated to 73° C. and the sulfonic acid (a) was added thereto over a period of 45 minutes. Stirring was continued for 90 minutes at 95° C. to 100° C. A separate flask was used for the reaction of a lime and water slurry (d+e) with the formaldehyde (f). Reaction was initiated at 65° C. by addition of approximately one-third of the formaldehyde; the remainder of the formaldehyde was added gradually at 80° C. so as to moderate the vigorously exothermic reaction. The acetic acid was then added dropwise at 70° C. to the lime, formaldehyde and water slurry. This mixed reagent was then placed in a dropping funnel for slow addition to the normal calcium sulfonate previously made. Hot water was used as rinse to complete the transfer of reagent. Addition of reagent took place over a period of 45 minutes. The product was dehydrated by use of a stream of nitrogen and a Dean-Stark water take-off. The temperature was raised to 105° C. in the course of 90 minutes and the product maintained at this temperature for 60 minutes. "Hyflo" (a diatomaceous earth filter aid) was used in the filtration, 4% admixed with the sample and 2% as a pre-coat on the electrically heated Buchner funnel. The oil filtrate recovered weighed 373 grams and had the following inspections:

Calcium-----	percent	12.25
Sulfur-----	do	1.39
Potentiometric base No., strong-----		9.1
Potentiometric base No., total-----		37
Viscosity @ 210° F., cs-----		57.35

¹196% excess metal, based on found normal salt value of 0.76% Ca.

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Example 2

Reactants:	Grams
(a) Sour oil A-----	400
(b) Lime, 96% (1.5 equivalents based on total N.N.)-----	12.4
(c) Water-----	28
(d) Lime, 96% (2.0 equivalents)-----	16.5
(e) Water-----	38
(f) Formaldehyde, 36% (2.4 equivalents)-----	43.0
(g) Acetic acid, glacial (0.6 equivalent)-----	7.72
(h) Water-----	20

Procedure.—Operations were substantially the same as with Example 1. The oil product recovered (slow filtration) weighed 378 grams and had the following inspections:

Calcium-----	percent	12.39
Sulfur-----	do	1.46
Potentiometric base No.-----		43
Viscosity @ 210° F., cs-----		69.22

¹214% excess metal, based on found normal salt value of 0.76% Ca.

Example 3

Reactants:	Grams
(a) Sour oil B-----	400
(b) Lime, 96% (1.6 equivalents base on total N.N.)-----	14.2
(c) Water-----	57
(d) Lime, 96% (3.6 equivalents)-----	32.0
(e) Water-----	96
(f) Formaldehyde, 36% (3.6 equivalents)-----	67.1
(g) Acetic acid, glacial (1.2 equivalents)-----	18.6
(h) Water-----	56

Procedure.—Operations were substantially the same as with Example 1. However, since gel-like particles appeared at the dehydration stage the material was treated with 100 grams of process oil (mineral oil, 100" SUV @ 100° F.) and 25 cc. of water. The material was dehydrated again and filtered in the usual manner. Product inspections were as follows:

Calcium-----	percent	12.57
Potentiometric base No., strong-----		4.4
Potentiometric base No., total-----		49
Viscosity @ 210° F., cs-----		57.23

¹315% excess metal, based on found normal salt [0.77% Ca] as corrected for dilution.

PREPARATION OF PETROLEUM OIL-WAX BENZENE SULFONIC ACID

In the following examples, 4, 5 and 6, a mixed petroleum-wax benzene sulfonic acid was employed as a substitute for the sour oils used in the previous examples. These petroleum-wax benzene sulfonic acids were prepared by the following procedure.

(a) **Preparation of wax benzene (2-12).**—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 occluded 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 complet-

ing 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.

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.

(b) *Preparation of mixed petroleum oil-wax benzene (2-12) sulfonate.*—Approximately 1000 grams of wax benzene (2-12), prepared in the manner described above, was charged to the sulfonator and the temperature thereof adjusted to 45° C. to 50° C. About 648 grams of oleum (25% SO₃) was fed into the wax benzene over a period of 1 to 1½ hours while the batch temperature was maintained at 50° C. to 55° C. with cooling water. Upon the completion of the oleum addition, approximately 2000 grams of a mineral oil (100" SUV at 100° F.) was added rapidly, the temperature adjusted to 50° C. to 55° C. and the batch stirred for one hour at this temperature. At the end of the stir period approximately 100 grams of water was added rapidly, allowing the exothermic heat of reaction to raise the temperature of the batch. The batch temperature was brought to about 70° C., agitation cut off and the batch allowed to settle for two hours. At the end of the settling period, the spent acid was drawn off and discarded. After the spent acid removal, the remaining sulfonated product was purified by agitation, aeration and centrifugation.

The resulting petroleum oil-wax benzene sulfonic acid, which was employed in Example 4, had a total N.N. of 47 and a true N.N. of 43. The petroleum oil-wax benzene sulfonic acids utilized in Examples 5 and 6 were similarly prepared, but showed slightly different neutralization numbers.

Example 4

Reactants:	Grams
(a) Petroleum-wax benzene sulfonic acid (total N.N. 47, true N.N. 43)-----	600
(b) Process oil (mineral oil, 100" SUV @ 100° F.)-----	150
(c) Lime, 96% (1.6 equivalents based on total N.N.)-----	31.1
(d) Water-----	125
(e) Formaldehyde, 36% (2.0 equivalents)---	84.0
(f) Acetic acid, glacial (0.5 equivalent)-----	15.1
(g) Lime, 96% (2.5 equivalents)-----	48.6

Procedure.—The mixture of acid and process oil (a+b) was added over the course of 60 minutes to the lime slurry (c+d) at 25° C. to 34° C. Acetic acid and formaldehyde (e+f) were added at room temperature, followed by the addition of dry lime (g). The emulsified reaction mixture was stirred for one hour at 35° C., then it was dehydrated to a final temperature of 155° C. to 160° C. "Hyflo" was used in the filtration, 4% admixed with the sample and 2% as a pre-coat on the electrically heated Buchner funnel. Product inspections were as follows:

Calcium-----percent---	12.92
Sulfur-----do-----	2.02
Potentiometric base No., strong-----	9.7
Potentiometric base No., total-----	57

¹173% excess metal, based on found normal salt of 1.07% Ca.

Example 5

Reactants:	Grams
(a) Petroleum-wax benzene sulfonic acid (total N.N. 49, true N.N. 43)-----	300
(b) Process oil (mineral oil, 100" SUV @ 100° F.)-----	112
(c) Lime, 96% (3.0 equivalents based on true N.N.)-----	27.2
(d) Water-----	136
(e) Lime, 96% (3.0 equivalents based on true N.N.)-----	27.2
(f) Formaldehyde, 36% (3.0 equivalents based on true N.N.)-----	57.5
(g) Acetic acid, Glacial (1.0 equivalent based on true N.N.)-----	13.8

Procedure.—The normal salt was prepared by addition of acid (a) over the course of 35 minutes to a stirred mixture of lime, water and process oil (c, d and b) at 70° C. Dry lime (e) was then added quickly, followed by formaldehyde (f). After a digestion period of one hour at 70° C. the acetic acid was added and dehydration was started. The dehydration was completed at 150° C. "Hyflo" was used in the filtration, 4% admixed with the sample and 2% as a pre-coat on the electrically heated Buchner funnel. Product inspections were as follows:

Calcium-----percent-----	13.51
Potentiometric base No., strong-----	14
Potentiometric base No., total-----	73
Formic acid content-----percent-----	1.49

¹268% excess metal, based on estimated normal salt value of 0.95% Ca.

Example 6

Reactants	Grams
(a) Petroleum-wax benzene sulfonic acid (total N.N. 47, true N.N. 42)-----	400
(b) Lime, 96% (1.6 equivalents based on total N.N.)-----	20.6
(c) Water-----	62
(d) Lime, 96% (2.4 equivalents)-----	31.0
(e) Formaldehyde, 36% (2.4 equivalents)---	67.2
(f) Acetic acid (0.8 equivalent)-----	16.1

Procedure.—The normal salt was prepared by rapid addition of acid (a) to a stirred slurry of lime and water, (b) and (c), at 70° C. After a digestion period of one hour dry lime (d) was added, then the formaldehyde and acetic acid mixture (e and f). An exothermic reaction occurred within a few minutes. At the end of an hour the dehydration was begun. Maximum dehydration temperature was 150° C. The product analysis showed as follows: Calcium, 4.61% (260% excess metal, based on estimated normal salt value of 1.28% Ca).

Example 7

Reactants:	Grams
(a) Sour oil C-----	300
(b) Ba(OH) ₂ ·8H ₂ O, 2.0 equivalents based on true N.N.-----	45.8
(c) Acetic acid, glacial, 0.8 equivalent based on true N.N.-----	7.0
(d) Formaldehyde, 36% 2.4 equivalents based on true N.N.-----	29.0
(e) Ba(OH) ₂ ·8H ₂ O, 3.0 equivalents based on true N.N.-----	68.7
(f) Water-----	137.5

Procedure.—The normal salt was prepared by addition of acid (a) over the course of 40 minutes to a mixture of base (b) and water (f) at 70° C. to 80° C. Further addition was made: first the acetic acid and formaldehyde (c+d), then the second portion of base (e). Slight exothermic action was noted. After a digestion period of one hour at 70° C. to 72° C. the dehydration was carried out as previously described. "Hyflo" was used in the filtration, 4% admixed with the sample and 2% as

a pre-coat on the electrically heated Buchner funnel. Product inspections were as follows:

Barium	percent.....	110.0
Potentiometric base No., strong.....		21
Potentiometric base No., total.....		52

¹ 202% excess metal based on estimated normal salt value of 3.31% Ba as calculated from 27 N.N.

ENGINE EVALUATION

To demonstrate the ability of the complex-formaldehyde-acetate-metal sulfonate salts of the invention as oil detergents, a series of oil blends thereof were prepared and tested in the CFR diesel D-21 and D-23 detergency tests. All of the additive salts were compared in an equivalent metal basis (0.088 weight percent for calcium). The additive oil blends also contained 1% of an antioxidant additive (pinene-P₂S₅ reaction product). This is common practice in evaluating oil detergents. The base oil used was an SAE 30 grade, solvent-refined, Mid-Continent oil (K.V. @ 100° F.=121 cs. and @ 210° F.=12.2 cs.). The test results are given in Table III.

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 CFR, 4-cycle, super-charged, Diesel engine is used. The operating conditions are as follows:

Oil temperature.....	° F..	175
Jacket temperature.....	° F..	212
Speed	r.p.m....	1800
Brake load.....	H.P....	7.5
Oil addition every 8 hours starting at 4 hours (1½ gallon sample used).		
Heat input.....	B.t.u./min....	1260

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 which 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.

DIESEL (D-23) DETERGENCY TEST

This test determines the effectiveness of a lubricating oil in preventing piston deposits and top ring wear. A single cylinder CFR, 4-cycle, super-charged diesel engine is used. The operating conditions are as follows:

Oil temperature.....	° F..	175
Jacket temperature.....	° F..	212
Speed	r.p.m....	1800
Brake load.....	H.P....	4.5

A 1½ gallon sample of oil is used at the start and oil is added every 8 hours starting at 4 hours. The duration of the test is 60 hours. The diesel fuel used contains 0.35% to 0.4% sulfur. The results are reported in terms of piston cleanliness ratings based on a scale ranging from 100 to 0 as in the D-21 test.

TABLE III

Additive	Percent By Weight	Percent Metal in Oil	CFR Diesel Test No.	Cleanliness Rating
None.....			D-21	65
None.....			D-23	82
None.....	1% Pinene-P ₂ S ₅ Product.		D-21	62
None.....			D-23	82
Example 1.....	3.91	Ca, 0.088	D-21	85
Example 2.....	3.72	Ca, 0.088	D-21	89
Example 3.....	3.42	Ca, 0.088	D-21	87
Example 4.....	3.00	Ca, 0.088	D-21	91
Example 5.....	2.5	Ca, 0.088	D-21	88
Example 6.....	1.91	Ca, 0.088	D-23	94
Example 7.....	3.00	Ba, 0.3	D-21	88

It is seen from the data that the high metal content complex salts of the invention are excellent engine oil detergents.

As indicated previously, the products of this invention

are actually oil solutions of the complex formaldehyde acetate metal sulfonate salts and although the products shown in the examples presented herein vary with respect to their complex salt contents, it will be understood that these differences can be eliminated by standardization of process procedure and/or adjustment of the products to some standard metal content, such as by final dilution with oil. The amount of product required to be added to a lubricating oil to provide the desired increase in detergent character thereof will, therefore, vary somewhat depending upon the process conditions utilized in preparing the particular product. In general, however, amounts ranging from about 0.1% to about 40%, by weight, may be used, the usual amount being from about 1% to about 10%.

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 oily 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.

This application is a continuation-in-part of application Serial No. 692,250, filed October 25, 1957, and now abandoned.

What is claimed is:

1. A method for preparing a complex metal salt of an oil-soluble sulfonic acid, said sulfonic acid being selected from the group consisting of petroleum sulfonic acids and alkyl-substituted aryl sulfonic acids the alkyl groups of which contain from about 8 to about 24 carbon atoms and said complex salt having a metal content of from about 200% to about 300% in excess of that of a normal metal salt of said sulfonic acid, which comprises the steps of (1) intimately contacting a hydrocarbon solution of the sulfonic acid in the presence of water with a hydroxide of a metal selected from the group consisting of calcium, barium and magnesium 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) forming a reaction mixture comprising the reaction product formed in step 1, formaldehyde, acetic acid and a hydroxide of a metal selected from the group consisting of calcium, barium and magnesium, in the presence of water, 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 acid-hydrogen in said sulfonic acid solution, the amount of acetic acid being from about 0.3 to 1.0 equivalent per equivalent of acid-hydrogen in said sulfonic acid solution, and the amount of metal hydroxide present in said reaction mixture 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 material from said reaction mixture.

2. A method for preparing a complex metal salt of an oil-soluble petroleum sulfonic acid, said complex salt having a metal content of from about 200% to about 300% in excess of that of a normal metal salt of said sulfonic acid, which comprises the steps of (1) intimately contacting an oil solution of the sulfonic acid, in the presence

of water, with a hydroxide of a metal selected from the group consisting of calcium, barium and magnesium, 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) forming a reaction mixture comprising the reaction product formed in step 1, formaldehyde, acetic acid and a hydroxide of a metal selected from the group consisting of calcium, barium and magnesium, in the presence of water, 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 acid-hydrogen in said sulfonic acid solution, the amount of acetic acid being from about 0.3 to 1.0 equivalent per equivalent of acid-hydrogen in said sulfonic acid solution, and the amount of metal hydroxide present in said reaction mixture being that sufficient to supply at least about 2 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 calcium salt of an oil-soluble petroleum sulfonic acid, said complex salt having a calcium content of from about 200% to about 300% in excess of that of a normal calcium salt of said sulfonic acid, which comprises the steps of (1) intimately contacting an oil solution of the sulfonic acid, in the presence of water, with about 1.5 to 2.0 equivalents of calcium hydroxide 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, acetic acid 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, the amount of calcium hydroxide being that sufficient to supply at least about 2 equivalents of calcium per equivalent of acid-hydrogen content in said sulfonic acid solution, and the amount of acetic acid being from about 0.3 to 1.0 equivalent per equivalent of acid-hydrogen 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 barium salt of an oil-soluble petroleum sulfonic acid, said complex salt having a barium content of from about 200% to about 300% in excess of that of a normal barium salt of said sulfonic acid, which comprises the steps of (1) intimately contacting an oil solution of the sulfonic acid, in the presence of water, with about 1.5 to 2.0 equivalents of barium hydroxide 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, acetic acid 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, the amount of barium hydroxide being that sufficient to supply at least about 2 equivalents of barium per equivalent of acid-hydrogen content in said sulfonic acid solution, and the amount of acetic acid being from about 0.3 to 1.0 equivalent per equivalent of acid-hydrogen 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 magnesium salt of an oil-soluble petroleum sulfonic acid, said complex salt having a magnesium content of from about 200% to about 300% in excess of that of a normal magnesium salt of said sulfonic acid, which comprises the steps of (1)

intimately contacting an oil solution of the sulfonic acid, in the presence of water, with about 1.5 to 2.0 equivalents of magnesium hydroxide 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, acetic acid and magnesium 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, the amount of magnesium hydroxide being that sufficient to supply at least about 2 equivalents of magnesium per equivalent of acid-hydrogen content in said sulfonic acid solution, and the amount of acetic acid being from about 0.3 to 1.0 equivalent per equivalent of acid-hydrogen 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 calcium salt of an oil-soluble wax-benzene sulfonic acid, said complex salt having a calcium content of from about 200% to about 300% in excess of that of a normal calcium salt of said sulfonic acid, which comprises the steps of (1) intimately contacting an oil solution of the sulfonic acid, in the presence of water, with about 1.5 to 2.0 equivalents of calcium hydroxide 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, acetic acid 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, the amount of calcium hydroxide being that sufficient to supply at least about 2 equivalents of calcium per equivalent of acid-hydrogen content in said sulfonic acid solution, and the amount of acetic acid being from about 0.3 to 1.0 equivalent per equivalent of acid-hydrogen 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 barium salt of an oil-soluble wax-benzene sulfonic acid, said complex salt having a barium content of from about 200% to about 300% in excess of that of a normal barium salt of said sulfonic acid, which comprises the steps of (1) intimately contacting an oil solution of the sulfonic acid, in the presence of water, with about 1.5 to 2.0 equivalents of barium hydroxide 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, acetic acid 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, the amount of barium hydroxide being that sufficient to supply at least about 2 equivalents of barium per equivalent of acid-hydrogen content in said sulfonic acid solution, and the amount of acetic acid being from about 0.3 to 1.0 equivalent per equivalent of acid-hydrogen 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.

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