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ORGANIC BARIUM COMPLEXES AND METHOD OF MAKING SAME

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This invention relates to organic metal complexes and novel methods of producing same. More particularly, the present invention relates to organic metal complexes which are derived from oil-soluble sulphonic acids and/or the barium salts thereof.

It is now recognized in the art that in preparing a salt or soap of an oil-soluble sulphonic acid, the use of an excess of neutralizing agent results in products which contain more metal than is theoretically required to form the normal salt or replace the acidic hydrogens of the sulphonic acid. The neutralizing agent employed for this purpose in the prior art, has been in the form of a metal oxide, hydroxide, carbonate, etc.

Work with this type of product has shown that for many uses, particularly where extreme care must be exercised to prevent the composition from being corrosive, as for example in lubricants, desirable results are secured by the use of so-called basic salts or soaps.

Among the earlier workers in the art who recognized this factor and indicated that the use of basic salts was desirable was Bergstrom, who in his patents, Nos. 2,270,577 and 2,279,086, made reference to the desirability of using the basic salts or soaps without, however, giving any specific method for the preparation of such materials. A similar disclosure is found in Van Ess Patent No. 2,372,411.

With the demonstrated superiority of such basic salts or soaps over the normal or slightly acidic soaps, the prior art workers then attempted to find ways of increasing the basicity of the soaps, or stated in another way, increasing the amount of metal, for example, held in stable form in what was termed as a metal complex. One of the earliest patents referring to these basic salts as complexes or coordination compounds is McNab, No. 2,418,894, who gives no indication in his patent as to the molecular structure of the product. As might be expected, one of the first steps employed to produce a metal salt having an intended large excess of metal in combination was to use an unusually large excess of neutralizing agent such as lime. A representative patent disclosing this procedure is Griesinger et al. No. 2,402,325, who suggested the use of neutralizing agent up to 220% of the theoretical amount. This large excess of neu-

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tralizing agent was employed in the process more or less conventional for producing salts or soaps, excepting that the process was carried out in the presence of steam to facilitate the formation of the product.

The work of Griesinger was followed by the work of Campbell and Dellinger as given in Patent No. 2,485,861. These patentees base their disclosure on the hypotheses that minor amounts of an alkaline earth metal hydroxide or carbonate can be peptized or held in a state of colloidal suspension in oil by means of an oil-soluble mahogany sulphonate. Another worker in the art who sought to combine in such complexes an excess amount of metal was Mertes whose Patent No. 2,501,737 was granted March 28, 1950. Mertes first prepared the normal salt and stated that such soap or soap concentrate "may have additional base combined therewith by a more or less simple mixing and heating operation followed by filtering." Mertes also indicates that his product is similar to that of Campbell and Dellinger, in that the excess neutralizing agent was held in the product in the form of a colloidal suspension.

All of the previously enumerated processes have been tried, not only duplicating certain of the examples given in the above-identified patents, but also using different acids and different neutralizing agents. As a result of these experiments, it has been found that there is a definite upper limit to the amount of barium metal which can be held in composition in colloidal suspension by means of these prior art processes. The greatest total amount of barium metal which can possibly be thus incorporated in the product by means of any of these prior art processes has been equal to about 2.3 times the theoretical amount present in the normal salt. For the purposes of the present invention, the ratio of the total metal in the complex to the amount of metal which is in the form of the normal salt of the oil-soluble sulphonic acid will hereinafter be referred to as the "metal ratio."

By means of the present invention, it is now possible to obtain barium organic complexes which contain more metal or higher metal ratios than is possible by prior art processes. With regard to lubricants, these high metal containing complexes are for example particularly suited as detergents, and by reason of the metal concen-

tration can be used in amounts appreciably less than other additives known in the prior art in order to attain a desired level of performance. It will also be observed that by virtue of the more effective nature of the present complexes in lubricants, usually it will cost less to obtain a desired result, because appreciably less additive is required. The barium organic complexes are produced in accordance with the present invention as a fluid, which is readily adapted for application where high concentrations of barium are desired, e. g., in lubricants. For example, if the complex alone is desired, it can be produced in mineral oil solutions of at least about 20% concentrations; whereas if the complex is wanted in combination with other additives, it can be available in concentrations of at least about 10% in mineral oils.

It is a principal object of this invention to provide a barium organic complex which contains in stable form an amount of metal substantially greater than that contained in any of the so-called barium metal complexes previously produced. It has been found that a metal ratio substantially greater than that possible with the prior art processes gives results which are strikingly superior, especially in the field of lubricants in which these products have particular utility.

It is a further object of this invention to produce by our improved process complexes which while containing the same amount of barium as complexes produced by the prior art processes above-described are nevertheless different from and superior to such prior art complexes.

Still another object of this invention is to provide novel methods of producing organic barium complexes.

Further objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

In its broadest aspects, the process of the present invention comprises combining an inorganic barium compound with an oil-soluble sulphonic acid and/or the barium salt thereof in the presence of a material which is referred to hereinafter as the "promoter." The precise function of the promoter material is not specifically understood since it has not been possible to specifically identify the molecular structure of the product produced. At present, it appears that none of the complexes, i. e., either those prepared by prior art techniques or those obtained under the present invention are susceptible of precise identification. This is clearly shown with respect to the prior art complexes by reason of the apparent disagreement among workers as to the nature of compounds which contribute metal in excess of the normal salt. In one instance, it is held that this phenomena is a result of partial replacement of the hydroxyl groups of the inorganic metal compound, whereas another group of prior art workers it is held that the high metal containing complexes are actually colloidal suspensions or dispersions in which the salt of the organic acid is the peptizing agent.

In the present invention the immediate product is produced by the use of a promoter and at least at one stage contains the promoter in chemical combination. It is possible, however, to recover the promoter from the product by suitable treatment as hereinafter explained and the final product, which then has a constitution different from the initial product, is similar to the initial product, of utility as a lubricant additive.

More particularly, the present invention comprises the process of producing a metal complex by combining an oil-soluble sulphonic acid and/or the barium salt thereof, a promoter, and an inorganic barium compound.

In a more specific aspect, the present invention is concerned with salt complexes which are prepared by the method comprising:

I. Preparing and mixing a mass in which, at 50° C., at least 50% of the components are in the liquid state, and in which mass the active components consist of:

A. An oil-soluble component selected from the class consisting of:

(1) The sulphonic acids;

(2) The barium sulphonates; and

(3) Mixtures of (1) and (2)

B. An organic compound containing an element of group VI of the periodic table having an atomic number less than 17, which compound is selected from the class consisting of:

(1) Organic compounds AH, in which H is hydrogen and A is an anionic radical, which compounds:

(*a*) Are water-soluble at a temperature of 50° C. to the extent of at least 0.0005%;

(*b*) In the presence of water at about 25° C. have an ionization constant greater than about 1×10^{-10}; and

(*c*) In saturated aqueous solutions at about 25° C. have a pH not greater than about 7;

(2) The barium salts of such organic compounds;

the relative amounts of A and B used being in the range of from about one equivalent of A to about 10 equivalents of B to about 10 equivalents of A to about 1 equivalent of B;

C. An inorganic barium compound;

(1) Which is water-soluble at a temperature of 50° C. to the extent of at least about 0.0003%; and

(2) In an amount such that there are present in the mass substantially more than one equivalent of barium, including the barium present in the remaining components, per equivalent of A plus B;

D. Water, including free and combined water in the other components, in an amount which is equal to at least one mole per mole of C.

II. And then maintaining the mass at a temperature and for a period of time sufficient to drive off substantially all free water and water of hydration which may be present.

Optionally, the above salt complex can be further modified by:

III. Treating the above mass with a sufficient amount of material which in the presence of the mass will form a material having a higher

ionization constant than the metal-free form of promoter, to liberate in the form of an ionizable organic compound, a substantial portion of the anionic radical of the compound B given above.

If desired, the salt complex prepared in accordance with Step III can then undergo treatment to:

IV. Remove from the mass so much of B(1) above as may have been regenerated by Step III.

The following examples give the preparation of a plurality of products which range in metal content from about that of the normal metal salt up to many times that amount.

We have found that sulphate ash and/or metal content values, and the metal ratio values calculated therefrom, are one of the most reliable means for characterizing certain of the salt complexes. As the description of the invention proceeds, it will become apparent that the neutralization number of a salt complex is in certain instances an unreliable index of the amount of excess metal in such complex, since it is greatly affected by the type of inorganic barium compound employed and can be varied within wide limits without significantly changing the metal content of the product by treatment of the mass with air, CO_2, or the like.

The above is not to be construed as a statement that the neutralization number is not an important property of a salt complex. For some uses, for example in lubricants, it is advantageous in certain instances to employ a salt complex of a substantially neutral character, whereas in other instances a salt complex of high alkalinity has been found to produce the desired results.

EXAMPLE 1

1980 grams of the barium salt of petrolatum sulphonic acid (which contains 9.2% sulphate ash and is derived from Pa. amber petrolatum) and 132 grams of para-tertiary-butyl phenol (ratio of equivalents of sulphonate to phenolic compound is 1.54), were placed into a 5-liter, 3-neck flask and heated to 95° C. To this mixture was added a barium oxide slurry (417 grams of barium oxide and 1100 grams of water) and the mixture was heated for about one hour at reflux temperature. Then the temperature was slowly raised to about 150–160° C. and maintained there for one hour to remove substantially all of the water. The product was then filtered. The salt complex is a viscous liquid, light brown in color, and having a very slight odor. The salt complex had the following properties:

Basic No.	23.1
Percent sulphate ash	13.96
Metal ratio	1.70

Solubility

Solvent	Percent of Product Added	Initial Appearance	Appearance after 1 Week	Appearance after 1 Month
Pa. 150 Neutral Oil	50	Clear	Clear	Clear
Do	10	Clear	Clear	Clear
Do	1	Clear	Clear	Clear

The above preparation, which is an example of the present invention, is compared with a basic sulphonate prepared in accordance with a conventional technique.

EXAMPLE 2

500 grams of the barium salt of the petrolatum sulphonic acid given in Example 1 where mixed with a slurry of barium oxide (containing 38 grams of barium oxide and 50 grams of water) and placed in a 2-liter, 3-neck flask, heated at about 160° C. for one hour until substantially all of the water was removed, and then the product is filtered. The resultant basic sulphonate has the following properties:

Basic No.	5.27
Percent sulfate ash	9.85
Metal ratio	1.08

EXAMPLE 3

100 grams of the barium salt of unsaturated paraffin wax sulphonic acid containing 13.1% sulfate ash were mixed with 455 grams of a mineral oil having a viscosity of 160 SSU at 100° F. and 109.5 grams of para-tertiary-butyl phenol (ratio of equivalents is 1.54), placed in a suitable vessel and heated to about 95° C. with stirring. To this mixture was added a slurry of barium oxide (containing 269 grams of barium oxide and 920 grams of water) and the total mixture was heated at about 100° C. for about one hour. The temperature was slowly raised to about 150° C. and held there for about one hour until substantially all of the water was removed. Then about 3% "Hyflo" (a filter-aid) was added to the product to facilitate filtering. The salt complex was then separated from the product by filtration. The salt complex thus prepared had the following properties:

Basic No.	53.8
Percent sulfate ash	26.5
Metal ratio	2.49

Solubility

Solvent	Percent of Product Added	Initial Appearance	Appearance after 1 Week	Appearance after 1 Month
Pa. 150 Neutral Oil	50	Clear	Clear	Clear
Do	10	Clear	Clear	Clear
Do	1	Clear	Clear	Clear

The salt complex product was fluid, brown in color, and did not contain any odor.

The preparation given in Example 3 is a typical illustration of the present invention. In Example 4 given below a basic sulphonate was prepared in accordance with a conventional technique for comparison with the product given in Example 3.

EXAMPLE 4

511 grams of the barium salt of unsaturated paraffin wax sulphonic acid given in Example 3 were mixed with 75 grams of water and heated to about 60° C. with stirring. 58 grams of barium oxide were added to the mixture which was then heated to about 150° C. and held there for one hour until substantially all of the water was removed. The product was then filtered with the aid of "Hyflo" in order to separate the complex salt. The salt complex possessed the following properties:

Basic No	16.2
Percent sulfate ash	19.7
Metal ratio	1.63

The salt was a waxy solid, brown in color, and did not contain any odor.

EXAMPLE 5

1000 grams of the barium salt of mono-paraffin wax substituted naphthalene sulphonic acid containing 8.63% sulfate ash were mixed with 445 grams of mineral oil having a viscosity of 160 SSU at 100° F. and 64.5 grams of para-tertiary butyl phenol (ratio of equivalents is 1.7) and heated to about 90° C. A slurry of barium oxide (203.5 grams of barium oxide and 543 grams of water) was added, and the mixture was heated for two hours at a reflux temperature of about 165° C. for a period of about one hour. "Hyflo" was then added to the product and the salt complex was recovered by filtration. The salt complex possessed the following:

Basic No	44.1
Percent sulfate ash	17.9
Metal ratio	2.37

The salt complex prepared in accordance with Example 5 was compared with a product which was made by a conventional technique, as shown in Example 6 below.

EXAMPLE 6

1000 grams of the barium salt of mono-paraffin wax substituted naphthalene sulphonic acid given in Example 5 were heated to about 95° C. and barium oxide slurry (115 grams barium oxide and 100 grams water) was added to the mixture. The total mixture was held at a temperature of 100° C. for about one hour, and then dehydrated at a temperature of about 150° C. for about one hour. The salt complex was separated by filtering the product. Throughout the above preparation a nitrogen atmosphere was maintained above the mixture. The resultant salt complex was liquid and black in color. The following properties were determined for the product:

Basic No	18.9
Percent sulfate ash	12.2
Metal ratio	1.45

EXAMPLE 7

400 grams of the barium salt of mono-paraffin wax substituted naphthalene sulphonic acid disulphide containing 8.2% sulfate ash and 27 grams of para-tertiary-butyl phenol (ratio of equivalents is 1.54) were placed in a suitable vessel and heated to 90° C. A barium oxide slurry constituting 66.5 grams of barium oxide and 180 cc. of water was added to the mixture and refluxed for about one hour. The temperature was then slowly raised to about 160° C. over a period of about four hours and held at that level for about 1.5 hours until substantially all of the water was removed. The salt complex was separated by filtering. The following properties were determined for the salt complex:

Basic No	69.7
Percent sulfate ash	24.3
Metal ratio	3.50

The product obtained in accordance with Example 7 was then compared with a salt complex obtained under a conventional technique as shown in Example 8 below.

EXAMPLE 8

20 ml. of water were added to 450 grams of the barium salt of mono-paraffin wax substituted naphthalene sulphonic acid disulphide given in Example 7 and heated to a temperature of about 60° C. 27.5 grams of barium oxide were then added to the mixture and the temperature was slowly raised to about 160–170° C. and held there for about one hour until substantially all of the water was removed. The salt complex was then separated by filtration. The product was fluid in consistency, black in color, and contained a slight odor. The following properties were determined for the product:

Basic No	5.27
Percent sulfate ash	8.95
Metal ratio	1.10

It is to be noted that the barium salt of mono paraffin wax substituted naphthalene sulphonic acid disulphide has a sulphate ash of about 8.2% and that the complex formed by the conventional technique did not increase the metal content appreciably. However, as shown in Example 7, the method of the present invention produces a complex containing substantially more metal in combination.

Other types of oil-soluble metal sulphonates were used in the method of the present invention. In the following examples, para-tertiary-butyl phenol was employed with different oil-soluble metal sulphonates. It is to be noted that in every instance a salt complex was formed containing more metal than is possible by known techniques.

EXAMPLE 9

6000 grams of a 30% by weight oil solution of barium petroleum sulphonate (sulphate ash content 7.6%) were mixed with 348 grams of para-tertiary-butyl phenol (ratio of equivalents 1.70) is a 12-liter, 3-neck flask and heated to 95° C. A slurry of barium oxide constituting 1100 grams of barium oxide and 2911 grams of water was then added and the mixture held for about one hour at a temperature of about 90–95° C. The total mixture was then slowly raised in temperature to 150° C. and dehydrated at that temperature over a period of about 4½ hours. The salt complex was separated by filtration and was found to be slightly viscous liquid, black in color, and did not contain any odor. The properties of the salt complex were as follows:

Basic No	72.1
Percent sulfate ash	23.1
Metal ratio	3.59

A mixture of different oil-soluble metal sulphonates was treated in accordance with a conventional technique and by the method of the present invention to determine what effect, if any, the two types of sulphonates would have on the quality of the product. Such preparations are given in Examples 10 and 11 below.

EXAMPLE 10

A mixture containing 500 grams of the barium salt of petrolatum sulphonate acid (sulfate ash 9.2%), 197 grams of the barium salt of petroleum sulphonic acid (sulfate ash 7.6%), and 50 grams of para-tertiary-butyl phenol (ratio of equivalents of sulphonate to phenolic material is 1.54) was heated to 95° C. A slurry of barium oxide constituting 123 grams of barium oxide and 330 grams of water was added to the mixture. The total mixture was refluxed for one hour at 100° C. and then the temperature was slowly raised to 150° C. for a period of one hour to substantially remove all the water. The complex was separated by filtration and was found to be a liquid,

and black in color. The following properties were determined:

Basic No.	27.7
Percent sulfate ash	17.25
Metal ratio	2.41

EXAMPLE 11

By the conventional technique, 480 grams of the barium salt of petrolatum sulphonic acid and 200 grams of the barium salt of petroleum sulphonic acid of Example 10 were mixed with a barium oxide slurry containing 68 grams of water and 60.8 grams of barium oxide. The components were heated to a temperature of 160° C. for one hour until substantially all the water was removed. The desired complex was separated by filtration and was found to be a viscous liquid, light brown in color, and contained a slight odor. The following properties were determined:

Basic No. 2	20.2
Percent sulfate ash	11.72
Metal ratio	1.51

The complexes of this invention can be also obtained by using a mixture of oil soluble organic acids and the barium salts thereof. The following example illustrates this concept.

EXAMPLE 12

2875 grams of petroleum sulphonic acid and 6000 grams of a 30% oil solution of barium petroleum sulphonate (sulphate ash is 7.6%) were mixed with 553.7 grams of para-tertiary butyl phenol (ratio of equivalents is 1.60). The mixture was heated to about 50° C. whereupon a slurry of BaO (consisting of 2027.6 grams of BaO and 5395 grams of water) was added and the mixture was then maintained at a temperature of about 90–95° C. for an additional hour. Upon inspection the mixture appeared thoroughly mixed, therefore the temperature was slowly raised to 150° C. and held there for approximately one hour. The product analyzed as follows:

Basic No.	73.0
Percent sulfate ash	23.3
Metal ratio	3.73

While most of the examples given herein use either a neutral or normal salt of the organic acid as a starting material to produce the high metal content complexes, nevertheless it is contemplated in this invention to employ as a starting material the overbased salts or complexes which are prepared according to conventional techniques. The following example illustrates this concept:

EXAMPLE 13

1634 grams of a barium petroleum sulphonate-BaO complex (obtained by dehydrating a barium petroleum sulphonate having a 7.6% sulfate ash, water, and BaO mixture at 150° C. for one hour, and producing a complex which has a basic number of 40, metal ratio of 2.25, and a 16% sulfate ash) and 121 grams of diisobutyl phenol (ratio of equivalents 1.7) were combined and heated to 70° C. To this mixture were added 665 cc. of water, followed by a slow addition of 175 grams of BaO. The entire mixture was then refluxed for one hour, and the temperature was raised to 150° C. over a 3 hour period and held there for one hour. Prior to filtering, the mass was blown with CO_2 at a rate of 3.6 cu. ft./hr. for 1½ hours at 150° C. The product analyzed as follows:

Basic No.	8.67
Percent sulfate ash	24.8
Metal ratio	4.13

It can be seen from the sulfate ash analysis of the product and the overbased sulphonate used as a starting material that there was an increase from 16.0% to 24.8% in sulfate ash. Clearly, therefore, the conventionally overbased sulphonates can be used as starting materials.

Other experiments were conducted in order to determine the effect of a higher dehydration temperature in the preparation of the salt complex of the present invention. In this respect, Examples 14 and 15 below illustrate the effect of higher temperatures.

EXAMPLE 14

2000 grams of a 30% oil solution of barium petroleum sulphonate (sulfate ash 7.6%) were mixed with 120 grams of para-tertiary butyl phenol (1.52 ratio of equivalents) and heated to 95° C. To said mixture was added a slurry of barium oxide containing 520 grams of barium oxide and 1390 ml. of water. The total mixture was heated for one hour at 100° C., and then was slowly raised in temperature over a period of three hours to 200° C. The mixture was maintained at this high temperature for a period of one-half hour. The salt complex was separated by filtering and was found to be an oily liquid, reddish-brown in color, and contained a faint odor. The following properties were determined:

Basic No.	71.5
Percent sulfate ash	24.3
Metal ratio	3.80

EXAMPLE 15

2035 grams of 30% oil solution of barium petroleum sulphonate (sulfate ash 7.6%) were mixed with 74.5 grams of phenol (1.67 ratio of equivalents) and heated to 100° C. A barium oxide slurry containing 483 grams of barium oxide and 1290 ml. of water was added and the mixture refluxed slowly for a period of one hour at 100° C. The mixture was then dehydrated by heating slowly to 200° C. and maintaining such a temperature for a period of about one-half hour. The salt complex was separated by filtration and was found to be an oily liquid, reddish-brown in color, and contained a slight odor. The following properties were determined for the complex:

Basic No.	111.5
Percent sulfate ash	32.8
Metal ratio	5.56

In addition to the promoters tested above, various other types were tried to determine the effectiveness thereof in forming salt complexes.

EXAMPLE 16

630 grams of a 30% oil solution of barium petroleum sulphonate (7.6% sulphate ash) were admixed with 350 grams of nitroparaffin wax (ratio of equivalents is 0.59). Then 760 cc. of water were added, followed by the addition of 296 grams of BaO. For one hour the mixture was agitated at 90–100° C., whereupon the temperature was raised to 150° C. and held at that level for one hour. The mixture was filtered,

and the complex obtained had the following properties:

Basic No.	132
Percent sulphate ash	33.3
Metal ratio	6.47

EXAMPLE 17

1500 grams of a 30% oil solution of barium petroleum sulphonate having a sulfate ash of 7.6%, 93 grams of iso-propyl phenol (ratio of equivalents 1.7) and 670 grams of water were placed in a 3-liter flask and heated to 60° C. 250 grams of BaO were then added, and the temperature was allowed to rise to 100° C. The mixture was held at 100° C. for one hour, followed by a rise in temperature to 150° C. over a 2 hour period, where the temperature was held for one-half hour. The total mixture was filtered, and the end-product had the following properties:

Basic No	87.8
Percent sulfate ash	25.95
Metal ratio	3.88

EXAMPLE 18

1140 grams of a 30% oil solution of barium petroleum sulphonate having a sulfate ash of 7.6% and 80 grams of paratertiary-amyl phenol (ratio of equivalents 1.54) were heated to 70° C. Thereafter 600 cc. of water were added, followed by a slow addition of 227 grams of BaO. The mixture was refluxed for one hour, and then the temperature was raised to 160° C. over a period of four hours and held there for one-half hour. The product was separated by filtration and had the following analyses:

Basic No	85.5
Percent sulfate ash	24.60
Metal ratio	3.96

EXAMPLE 19

2583 grams of a 30% oil solution of barium petroleum sulfonate having a 7.6% sulfate ash, 144.2 grams of beta-naphthol (ratio of equivalents is 1.69) and 1262 ml. of water were combined and mixed thoroughly. Then 472 grams of BaO were added over a 1 hour period, followed by maintaining the total mixture at 100° C. for 1 hour. The temperature was then raised to 150° C. and held there for 1 hour. Prior to filtering the mixture, it was blown with CO_2 for 75 minutes at which time the mixture had a basic number of 0.8. After filtering, the product analyzed as follows:

Basic No	4.88
Percent sulphate ash	23.8
Metal ratio	3.90

EXAMPLE 20

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash, 129 grams of iso-nonyl phenol (ratio of equivalents is 1.7) and 727 ml. of water were combined and thoroughly mixed. Then 271 grams of BaO were added and the total mixture was held at 100° C. for 1 hour. The temperature was then raised to 150–160° C. and held there for 1 hour. Prior to filtering, the mass was blown at about 150° C. with CO_2 until a basic number of about 1 was obtained. The filtered product analyzed as follows:

Basic No	3.9
Percent sulphate ash	25.0
Metal ratio	4.17

EXAMPLE 21

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash, 215 grams of tertiary-butyl chlorophenol (ratio of equivalents is 1.7), and 1265 cc. of water were combined, followed by an addition of 459 grams of BaO. The temperature of the total mixture was raised to 100° C. and held there for 1 hour. Then the temperature was raised to 150° C. where it was held for 1 hour. Prior to filtering the mixture, it was blown for 3 hours with CO_2 at 135°–145° C. until the mixture was slightly basic. The filtered product analyzed as follows:

Basic No	13.3
Percent sulfate ash	25.45
Metal ratio	4.38

EXAMPLE 21

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash, 215 grams of tertiary-butyl chlorophenol (ratio of equivalents is 1.7), and 1265 cc. of water were combined, followed by an addition of 459 grams of BaO. The temperature of the total mixture was raised to 100° C. and held there for 1 hour. Then the temperature was raised to 150° C. where it was held for 1 hour. Prior to filtering the mixture, it was blown for 3 hours with CO_2 at 135°–145° C. until the mixture was slightly basic. The filtered product analyzed as follows:

Basic No	13.3
Percent sulfate ash	25.45
Metal ratio	4.38

EXAMPLE 22

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash and 210 grams of trichlorodiphenyl ether sulphonic acid (ratio of equivalents is 1.7) were heated to 70° C. To this mixture were added 725 grams of water, followed by the addition of 271 grams of BaO. The entire mixture was refluxed for 1 hour, then heated to 150° C. over a 3 hour period and held there for 1 hour. Prior to filtering, the mixture was blown with CO_2 at 150° C. and at a rate of 3.6 cu. ft./hr. for 1½ hours. The filtered product analyzed as follows:

Basic No	0.45
Percent sulfate ash	24.7
Metal ratio	4.34

EXAMPLE 23

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash and 175 grams of tertiary-butyl naphthalene sulphonic acid (ratio of equivalents is 1.7) were combined and heated to 70° C. To this mixture were added 725 grams of H_2O, followed by a slow addition of 271 grams of BaO. The entire mixture was then refluxed for one hour, and then heated to 150° C. over a 3 hour period. The mixture was held at 150° C. for 1 hour. Prior to filtering, the mass was blown at 150° C. with CO_2 at a rate of 3.6 cu. ft./hr. for 1½ hours. The filtered product analyzed as follows:

Basic No	0.41
Percent sulfate ash	24.1
Metal ratio	4.12

EXAMPLE 24

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash and 131 grams of methyl naphthalene sulfonic

acid (ratio of equivalents is 1.7) were combined and heated to 70° C. 725 grams of water were added to the mixture, followed by a slow addition of 271 grams of BaO. The entire mixture was refluxed for 1 hour, then the temperature was raised to 150° C. over a three hour period, and held there for one hour. Prior to filtering, the mass was blown with CO_2 at a rate of 3.6 cu. ft./hr. for 1½ hours at 150° C. The filtered product analyzed as follows:

Basic No	Nil
Percent sulfate ash	25.9
Metal ratio	4.41

EXAMPLE 25

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash, 113 grams of diisobutenyl sulphonic acid (ratio of equivalents is 1.7) and 725 grams of H_2O were combined and heated to 70° C. To this mixture were added 271 grams of BaO, and the entire mixture was heated at 100° C. for 1 hour. The mixture was then heated at 150° C. for one hour, followed by blowing with CO_2 at 150° C. prior to filtering, to obtain a substantially neutral mass. The filtered product analyzed as follows:

Basic No	0.23
Percent sulfate ash	24.6
Metal ratio	4.10

EXAMPLE 26

Di-isopropyl benzene sulphonic acid, obtained by reacting 162 grams of di-isopropyl benzene with 122 grams of chloro sulphonic acid for 1 hour at 100° C., was combined with 2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash and 1220 ml. of water. The ratio of equivalents of oil soluble sulphonate to sulphonic acid is 1.7. Then 461 grams of BaO were added slowly and the mixture held at 100° C. for 1 hour. The temperature was raised to 150° C. and held there for 1 hour. Prior to filtering, the mixture was blown with CO_2 for ½ hour at 120–140° C. The filtered product analyzed as follows:

Acid No	1.22
Percent sulfate ash	25.4
Metal ratio	4.3

EXAMPLE 27

Cymene sulfonic acid, obtained by reacting 134 grams of cymene with 122 grams of chlorosulphonic acid at 70–100° C. for 1½ hours, was combined with 2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash and 1220 ml. of water. The ratio equivalents of oil soluble sulphonate to sulphonic acid is 1.7. To this mixture were added 461 grams of BaO, and the entire mixture was then held at 85–100° C. for 1 hour. Then the temperature was raised to 150° C. and held there for 1 hour. Prior to filtering, the mass was blown with CO_2 for ½ hour at 130° C. The filtered product analyzed as follows:

Acid No	0.95
Percent sulfate ash	25.8
Metal ratio	4.38

EXAMPLE 28

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash, 2219 grams of tertiary-butyl dichlorophenol (ratio of equivalents is 1.7) and 1265 grams of water were combined, followed by an addition of 459 grams of BaO over a 45 minute period. The entire mixture was held at 100° C. for 1 hour, followed by maintaining the temperature at 150° C. for 1 hour. Prior to filtering, the mass was blown with CO_2 for 90 minutes at 135–150° C. until the mass was slightly acidic. The filtered product analyzed as follows:

Basic No	6.45
Percent sulfate ash	23.2
Metal ratio	3.85

EXAMPLE 29

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash, 236 grams of di-isopropyl dithiophosphoric acid (ratio of equivalents is 1.7) and 1220 ml. of water were combined, followed by a slow addition of 461 grams of BaO. The mixture was held at 100° C. for 1 hour, and then heated to 150° C. and held there for 1 hour. Prior to filtering, the mass was blown with CO_2 for 20 minutes at 125–150° C. The filtered product analyzed as follows:

Acid No	0.27
Percent barium	14.25
Percent sulfate ash (calculated from metal content)	24.2
Metal ratio	4.15

EXAMPLE 30

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash, 100 grams of acetyl acetone (ratio of equivalents is 1.7) and 1265 cc. of water were combined, followed by a slow addition of 459 grams of BaO over a 1 hour period. The entire mixture was held at 94° C. for 1 hour, followed by a 1 hour period of heating at 150° C. Prior to filtering, the mass was blown with CO_2 for 1 hour at 135°–150° C. The filtered product analyzed as follows:

Acid No	0.2
Percent sulfate ash	22.8
Metal ratio	3.48

EXAMPLE 31

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash and 206 grams of di-t-butyl naphthalene sulphonic acid (ratio of equivalents is 1.7) were combined and heated to 70° C. 725 grams of water were then added, followed by a slow addition of 271 grams of BaO. The mixture was refluxed for 1 hour, and then held at 150° C. for 1 hour. Prior to filtering, the mixture was blown with CO_2 at a rate of 3.6 cu. ft./hr. for 1.25 hours at a temperature of 150° C. The filtered product analyzed as follows:

Acid No	0.24
Percent sulfate ash	23.6
Metal ratio	4.12

EXAMPLE 32

A mixture of 2280 grams of a 30% oil solution of barium petroleum sulphonate (sulfate ash 7.6%) and 83 grams of phenol (ratio of equivalents is 1.53) was heated to a temperature of 60° C. 496 grams of barium oxide and 1300 grams of water were added to the above mixture and the temperature was raised to 90–100° C. After holding at said temperature for one hour, the temperature was raised over a period of three hours to 150° C., and held at that level for ½

hour. The resultant salt complex was fluid in consistency and dark red in color. The following properties were determined:

Basic No	91.4
Percent sulfate ash	26.8
Metal ratio	4.37

EXAMPLE 33

The promoter employed in this test was prepared by reacting 80 grams of tertiary butyl benzene with 71 grams of chlorosulphonic acid at a temperature of 30–40° C. for a period of one hour. The resultant product, tertiary butyl benzene sulphonic acid, was dissolved in a little warm water and admixed with 1550 grams of a 30% oil solution of barium petroleum sulphonate (ratio of equivalents of sulphonate to sulphonic acid is 1.52). The mixture was heated to 90° C., whereupon 284 grams of barium oxide and 260 ml. of water were added. The mixture was stirred for one hour at a temperature of 100–102° C. The temperature was thereupon raised to 200° C. for a short period and then reduced to 150° C. and held at that level for a period of one hour. The salt complex thus obtained was an oily liquid, reddish-brown in color, and contained a faint odor. The properties of the product are as follows:

Basic No	64.7
Percent sulfate ash	27.0
Metal ratio	4.73

EXAMPLE 34

2500 grams of 30% oil solution of barium petroleum sulphonate (sulfate ash 7.6%) were admixed with 173 grams of para-tertiary butyl benzoic acid (1.68 ratio of equivalents) and heated to 95° C. 458 grams of barium oxide and 1215 grams of water were added to the mixture and the temperature was maintained at 100° C. for about one hour. Thereafter the temperature was slowly raised to 150° C. and maintained at that level for a period of one hour. The salt complex was filtered from the total mixture and was an oily liquid, brown in color, and contained a faint odor. The following properties were determined:

Basic No	32.1
Percent sulfate ash	19.1
Metal ratio	2.88

EXAMPLE 35

2050 grams of a 30% oil solution of barium petroleum sulphonate (sulfate ash 7.6%) were admixed with 73.5 grams of 1-nitro propane (ratio of equivalents is 1.62) and heated to a temperature of 95° C. 388 grams of barium oxide and 1035 ml. of water were added to the mixture and the temperature was maintained for a period of one hour at 100° C. Thereafter the temperature of the mixture was slowly raised to 150° C. over a period of 2½ hours and maintained at that level for a period of one hour. The product was filtered to separate the salt complex. The desired product was an oily liquid, reddish-brown in color, and contained a slight odor. The following properties were determined for the product:

Basic No	78.2
Percent sulfate ash	28.2
Metal ratio	4.60

Another experiment was performed in which the promoter was in the salt form. Example 36 below illustrates this feature of the invention.

EXAMPLE 36

1700 grams of a 30% oil solution of barium petroleum sulphonate (sulfate ash 7.6%) were admixed with 105 grams of barium phenate (ratio of equivalents is 1.7) and 570 grams of water. The mixture was heated to 75–100° C. whereupon 214 grams of barium oxide were added. The temperature of the mixture was maintained at 100° C. for one hour and then raised slowly to 150° C. and held at this level for a period of one hour. The salt complex was then separated from the product by filtration and was found to be a viscous liquid, light brown in color, and contained a slight odor. The following properties were determined for the salt complex:

Basic No	68.
Percent sulfate ash	21.4
Metal ratio	3.23

The salt complex can also be prepared by starting with the oil-soluble sulphonic acid and combining therewith the promoter and the inorganic metal compound. This technique differs from those given above, because as shown in all the above examples, the normal metal sulphonate was employed as a starting material. In order to demonstrate that the metal ratio of the salt complex obtained by this method is greater than by conventional techniques, a comparison was made therewith, in which experiments the acid was employed as a starting material. In this respect, Examples 37 and 38 below are illustrative.

EXAMPLE 37

The oil-soluble petroleum sulphonic acid employed in this test was derived by reacting a 60% oil solution of sodium petroleum sulphonate with the stoichiometric amount of sulfuric acid (96% strength) at a temperature of 60–70% C. for a period of two hours. After allowing the mixture to stand for about 12 hours, it was filtered twice through a glass cloth. 2875 grams of the product just described were combined with 205.7 grams of tertiary butyl phenol (ratio of equivalents is 1.39), 1647 grams of low viscosity mineral oil having a viscosity of about 120 SUS at 100° F., 927.6 grams of barium oxide and 2480 grams of water and heated for one hour at a temperature of 98° C. The mixture was then dehydrated for one hour at a temperature of 150° C. so as to remove substantially all of the water. The product was a viscous liquid, brown in color, and contained a mild odor. The following properties were determined for the desired product:

Basic No.	74.2
Percent sulfate ash	24.4
Metal ratio	4.02

EXAMPLE 38

500 grams of the oil-soluble petroleum sulphonic acid given in Example 37 above were heated to 75° C. 55 grams of water were then added and followed by a slow addition of 162.2 grams of barium oxide. The total mixture was maintained at a temperature of 150° C. for a period of one hour. The desired complex was separated by filtration and was found to be a very viscous liquid, black in color and did not contain any odor. The following properties were determined for the product:

Basic No.	53.7
Percent sulfate ash	25.65
Metal ratio	1.74

It was indicated hereinabove that the salt complexes of the present invention can be prepared by first adding water to the mixture of the oil-soluble metal sulphonate and/or sulphonic acid and promoter, and then adding the inorganic metal compound in a dry state. In this respect, Example 39 given below illustrates an alternative method by which the salt complex can be prepared.

EXAMPLE 39

1000 grams of the barium salt of diparaffin wax substituted phenol sulphonic acid (sulfate ash 6.6%) were admixed with 55 grams of para-tertiary butyl phenol (ratio of equivalents is 1.54) and heated to a temperature of 90° C. 800 cc. of water were then added. The mixture was mixed thoroughly and then 300 grams of dry barium oxide were added. The total mixture was refluxed for two hours followed by an addition of 573 grams of a mineral oil having a viscosity of 160 SSU at 100° F. The temperature was raised over a period of four hours to 170° C. and then maintained there for one hour. The salt complex was obtained by filtering the product and was found to be a viscous liquid, dark brown in color, and contained a faint odor. The properties of the salt complex are as follows:

Basic No.	67.8
Percent sulfate ash	23.8
Metal ratio	2.67

Another method of preparing the organic barium complexes is to treat the mass, prior to filtering, with an acidic material, and then filtering same to recover the desired metal complex. The steps of preparation, prior to treating with the acidic material, can be any of those discussed herein. The following examples illustrate such a method of producing the complex and serve as a comparison to show the improvement over methods of preparation not employing the treating step with the acidic material.

EXAMPLE 40

1700 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash were mixed with 134 grams of diisobutyl-phenol (ratio of equivalents is 1.7) and heated to 70° C. 302 grams of BaO and 800 cc. of water were then added to the mixture, and the total mass was refluxed for 1 hour. The temperature was then raised to 160° C. over a period of 6 hours and maintained at that temperature for one hour. The mixture was filtered and the complex obtained. The following properties of the product were determined:

Basic No.	66.0
Percent sulfate ash	22.2
Metal ratio	3.64

EXAMPLE 41

1700 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash were mixed with 134 grams of diisobutyl-phenol (ratio of equivalents is 1.7) and heated to 70° C. 302 grams of BaO and 800 cc. of water were then added thereto, and the total mixture refluxed for about 1 hour. The temperature was then raised to 150° C. over a period of 1¾ hours, and held at that level for 1 hour. The mixture was then blown with CO_2 at a temperature of 150° C. and at a rate of 1650 cc./minute for 38 minutes, and the mixture possessed a basic No. of 1.47. The mixture was then filtered and the desired complex obtained. The following properties were determined:

Basic No.	5.05
Percent sulfate ash	26.0
Metal ratio	4.52

From the two examples given above it can be seen from the sulfate ash analyses of the products that CO_2 blowing prior to filtering increased the metal content significantly.

The example below illustrates the utility of SO_2 in this respect.

EXAMPLE 42

4590 grams of a 30% oil solution of barium petroleum sulphonate having a sulfate ash of 7.6% were mixed with 363 grams of diisobutyl-phenol (ratio of equivalents is 1.7) and 2800 grams of water and heated to 60° C. About 1042 grams of BaO were then added and the temperature was raised to 94–98° C. and held there for 1 hour. The temperature was then raised to 150° C. over a 4 hour period and maintained at that level for 1 hour. About 316 grams of the total mixture were removed and the product obtained by filtering, product A, contained the following analysis:

Product A

Basic No	63.0
Percent sulfate ash	19.5
Metal ratio	3.18

The remainder of the unfiltered mass, about 5296 grams, was blown with about 330 grams of SO_2 at about 170° C., and until the mass was slightly acidic. The total weight gain of the mass was 206 grams. The mixture was then filtered and the product identified as product B contained the following analysis:

Product B

Basic No	4.5
Percent sulfate ash	29.0
Metal ratio	5.35

Clearly, the increase in metal content by virtue of treating with SO_2 is from 19.5 to 29.0% on a sulfate ash basis.

As mentioned hereinabove, the salt complexes can also be prepared by combining the oil-soluble metal sulphonate and inorganic metal compound in the presence of the sediment which forms occasionally in some of the methods illustrated above. The following examples illustrate the utility of the sediment for preparing salt complexes for the present invention.

EXAMPLE 43

1700 grams of 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash were mixed with 61 grams of phenol (ratio of equivalents is 1.70) and the mixture was heated to 75° C. 261 grams of barium oxide and 710 grams of water were then added and the total mixture was raised in temperature to 100° C. and held at that level for one hour. Thereafter, the temperature was raised slowly to 150° C. and held there for about one hour. The total mixture was allowed to settle overnight, followed by decantation and filtering. In this experiment 450 grams of sediment were produced. The salt complex was a viscous liquid, light brown in color and contained a slight odor. The following properties of the product were determined:

Basic No	59.5
Percent sulfate ash	21.2
Metal ratio	3.20

The sediment obtained in Example 43 was employed in the preparation of a salt complex in the method given in the following example No. 44.

EXAMPLE 44

1700 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulfate ash, 20 grams of phenol, 450 grams of sediment obtained from the preparation given in Example 43, 710 grams of water and 261 grams of barium oxide (barium oxide added slowly) were mixed together and heated to a temperature of 100° C. for about one hour. The total mixture was then raised in temperature in a slow manner to about 150–160° C. and held there for one hour until substantially all the water was removed. The salt complex was separated by filtration and was found to be a viscous liquid, light brown in color, and contained a slight odor. The following properties were determined for the salt complex:

Basic No	82.6
Percent sulfate ash	26.4

The salt complexes formed with oil soluble petroleum sulphonic acid compounds possess exceptionally high metal ratios as compared to those complexes which are obtained when using other oil soluble organic acids. Consequently, in determining the maximum amount of barium metal which can be incorporated into a complex prepared by conventional techniques, the barium petroleum sulphonate was employed for such a purpose. Pursuant thereto, Examples 45 and 46 given below serve to show the highest amount of barium metal which can be incorporated into a salt complex by a conventional technique.

EXAMPLE 45

2500 grams of a 30% oil solution of barium petroleum sulphonate containing 7.6% sulfate ash were heated to 95° C. and a slurry of barium oxide containing 386 grams of barium oxide and 1215 grams of water was added thereto. The mixture was stirred for one hour at a temperature of 100° C. and then heated slowly over a period of three hours to a temperature of 150° C. This temperature was maintained for about one hour until substantially all the water was removed. The salt complex thus produced had the following properties:

Basic No	38.4
Percent sulfate ash	16.0
Metal ratio	2.25

EXAMPLE 46

In this example the procedure employed in Example 45 was followed except that the dehydration step was conducted at a temperature of 200° C. for a period of ½ hour. The product obtained had the following properties:

Basic No	29.0
Percent sulfate ash	15.3
Metal ratio	2.16

From the above Examples 45 and 46, it can be seen that salt complexes obtained by conventional techniques will only contain a barium metal ratio as high as 2.25 or approximately 2.3. By comparison, the product obtained in accordance with the present invention will in every instance wherein a substantial amount of excess inorganic barium compound is employed, produce products containing more metal than is possible by conventional techniques. Therefore, in every instance where the salt complex is treated with an acidic material and then distilled so as to remove substantially all of the promoter material, the remaining salt complex which constitutes essentially the combination of promoter-free salt complex and the acidic material will have a higher ratio of total metal to normal salt of sulphonic acid than is possible under conventional techniques. In the examples given hereinafter, it will be shown that the treatment of a salt complex with an acidic material does not significantly effect the metal content of the complex. Furthermore, it will be shown in those examples that the distillation of the acidic material treated complex to recover the promoter does not effect the metal content of the complex.

In another pair of experiments, a comparison was made between the process of the present invention and a conventional process, when using duplicate amounts of components. It is clearly evident from the following examples that this invention will give substantially better results with respect to metal concentration of the complex than is obtainable by the conventional technique.

EXAMPLE 47

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash, 88 grams of para-tertiary butyl phenol (ratio of equivalents is 1.7), 271 grams of BaO and 725 ml. of water were mixed together at 60–70° C. The temperature of the mixture was raised to 100–105° C. and held there for one hour while insuring thorough mixing. Thereafter the temperature was raised to 150–160° C., and held at that level to remove substantially all the water. The complex was separated by filtration and had the following analyses:

Basic No	85.2
Percent sulfate ash	25.5
Metal ratio	4.12

EXAMPLE 48

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash were mixed with 725 ml. of water at about 60° C. Then 271 grams of BaO were added. The temperature of the mixture was raised to 100–105° C. and held there for one hour while insuring thorough mixing. Thereafter the temperature was raised to 150–160° C. and held there for one hour to substantially remove all the water. The complex was separated by filtration and had the following properties:

Basic No	36.0
Percent sulfate ash	15.34
Metal ratio	2.14

In all of the foregoing examples, the ratio of equivalents of the organic acid or salt thereof to the promoter has been within the preferred range, viz. 1.5–3.5 to 1. The following examples illustrate the preparation of end-products wherein the ratio of equivalents falls outside of said preferred range, but comes within the broad range found to be operable.

EXAMPLE 49

1000 grams of a 30% oil solution of barium petroleum sulphonate containing 7.6% sulphate ash were mixed with 750 grams of water at 50° C. 282 grams of BaO were added thereto, followed by the addition of a slurry consisting of 460 grams of water, 87 grams of BaO, and 115 grams of para-tertiary-butyl phenol (ratio of equivalents of sulphonate to phenolic compound is

0.77). The mass was stirred for ½ hour at about 100° C., then it was heated to 200° C. and maintained at that temperature for 2 hours.

The salt complex was separated by filtration. It was a red-brown, viscous liquid, and had the following properties:

Basic No	46
Percent sulfate ash	27.9
Metal ratio	5.4

EXAMPLE 50

2760 grams of a 30% oil solution of barium petroleum sulphonate containing 7.6% sulphate ash were mixed with 217 grams of BaO, 580 grams of water and 41 grams of diisobutenyl sulphonic acid in that order. The ratio of equivalents of sulphonate to sulphonic acid is 9.

The mass was heated for one hour at about 100° C., then the temperature was raised to 150° C. and maintained there for one hour. The salt complex was separated by filtration. It was a viscous, brown liquid, and had the following properties:

Basic No	34
Percent sulfate ash	17.3
Metal ratio	2.4

As previously indicated, the immediate product formed by the use of the promoter material may be modified to recover therefrom a substantial portion of the promotor material used by treating such immediate product with a sufficient amount of an acidic material which in the presence of the mass will form a material having a higher ionization constant than the promoter used in the preparation of the immediate product. The promotor is liberated in the form of an organic compound AH containing a substantial portion of the anionic radical of the promotor material. After a portion of the promotor material has been thus regenerated by treating the immediate product with an acidic material, the regenerated promotor may then be separated therefrom by any one of the several known means, or the regenerated promotor material may be left in the mass and the latter then treated with an additional amount of a salt-forming material, and it will be found that the concentration of the stably held metal can be further increased. The following are examples of such further steps in our process.

EXAMPLE 51

The salt complex produced in Example 39 was mixed with 1239 grams of mineral oil and heated to a temperature of 190° C. While maintaining this temperature for a period of 1½ hours, CO_2 was blown through the mixture. The temperature was then lowered to 150° C. continuing the passage of CO_2 through the mixture and the basic number of the mixture was tested every 10 minutes, until the analysis showed a basic number of 2.5. The salt complex CO_2 product was then separated and was found to be liquid in consistency, brown in color, and contained a very slight odor. The following properties were determined for the product:

Basic No	2.5
Percent sulfate ash	23.2

By comparison, the product of Example 38 contained a sulphate ash of 23.8% whereas this same product after blowing with CO_2 contained a sulphate ash of 23.2. Therefore, it can be seen that the metal content of the salt complex is substantially the same after treatment with CO_2.

EXAMPLE 52

6043 grams of the salt complex prepared in accordance with Example 9 were placed in a suitable vessel and CO_2 gas was injected at the bottom of the vessel at a rate of 3750 cc. per minute for a period of $1\frac{1}{6}$ hours. During this period, the temperature was in the range of 30–70° C. At the end of the blowing operation the product weighed 6346 grams, showing a gain in weight of 303 grams. The product was fluid, dark red in color, and contained no odor. The following properties were determined for the salt complex-CO_2 product:

Basic No	4.3
Percent sulfate ash	22.7

It can be seen, therefore, by the gain in weight of the product that the CO_2 actually enters into combination with the salt complex. Furthermore, the metal content of the product is substantially the same as the salt complex prior to being blown with CO_2, since the sulfate ash content is substantially the same as before CO_2 treatment.

EXAMPLE 53

1288 grams of the salt complex prepared in accordance with the method of Example 5 were blown with CO_2 at a temperature of 30–50° C. until the product showed an acid reaction. Following this CO_2 treatment, the product was blown with nitrogen for a period of 15 minutes. The product thus produced was very viscous, reddish-brown in color, and did not contain any odor. The following properties were determined:

Acid No	5.36
Percent sulfate ash	17.94

The above examples clearly show that it is possible to treat the salt complex with an acid anhydride gas and obtain a product which is definitely acid. Further, treatment with an acid anhydride gas to such extent does not change the metal content of the salt complex.

Another salt complex product which was blown with CO_2 is given in Example 54 below:

EXAMPLE 54

2500 grams of a 30% oil solution of barium petroleum sulphonate containing 7.6% sulfate ash were mixed with 45.6 grams of phenol, (ratio of equivalents is 3.36) and heated to 95° C. A slurry of barium oxide containing 422 grams of barium oxide and 1125 ml. of water was added to the mixture, with stirring, and held at a temperature of 97–102° C. for a period of one hour. The temperature was then slowly raised over a period of three hours to 150° C. and maintained at that level for an additional period of one hour until substantially all the water was removed. The desired salt complex was separated by filtering and was found to be an oily liquid, brown in color, and contained a faint odor. The following properties were determined:

Basic No	60.6
Percent sulfate ash	22.3
Metal ratio	3.34

EXAMPLE 55

1250 grams of the salt complex produced in accordance with the method given in Example 54 above were blown with CO_2 for approximately two hours at a temperature below 60° C., until an acid number of 5.0 was obtained. The weight of product obtained was 1260 grams.

The CO_2-salt complex product was then heated at a temperature of 190° C. under a vacuum of 10 mm., producing a distillate weighing about 10 grams. The distillate was then dissolved in iso-propyl ether and then dried over sodium sulphate, filtered and then the sulphate was removed by evaporation. 5 grams of residue remained. This residue was found to be mostly phenol, thus indicating that treatment of the salt complex with an acidic material dissociates at least a portion of the promoter from complex formation.

After the distillation step, the following properties for the salt complex were determined:

Basic No.	2.96
Percent sulfate ash	22.4

The percent sulphate ash of the CO_2-salt complex product indicates that little or no metal is removed from the complex as a result of the CO_2 treatment and the distillation step to recover the promoter.

EXAMPLE 56

1440 grams of the salt complex obtained by the method given in Example 43 were blown with CO_2 for about two hours at a temperature of 30–60° C. until the product showed an acid No. of 6. The product thus obtained was then heated at a temperature of 200° C. under vacuum of 4 mm. to recover approximately 15 grams of phenol. The residue of the distillation was a viscous liquid, light brown in color, and containing a slight odor. This product possessed the following properties:

Basic No.	1.06
Percent sulfate ash	22.6

Here again, it is shown that the treatment of the salt complex with an acidic material dissociates the promoter from complex formation in the salt. On a quantitative basis, it was determined that approximately ⅓ of the original phenol was still held in complex formation in the CO_2 treated product.

The salt complex prepared in accordance with Example 57 below was treated with SO_2 as shown in Example 58 which is also given below.

EXAMPLE 57

6000 grams of a 30% solution of barium petroleum sulphonate (sulfate ash 7.6%), 348 grams of para-tertiary butyl phenol (ratio of equivalents is 1.70), and 2915 grams of water were mixed and heated to a temperature of 60° C. 1100 grams of barium oxide were added slowly and the temperature of the total mixture was raised to 94–98° C. and held there for one hour. The temperature of the mixture was then slowly raised over a period of 7½ hours to about 150° C. and held at that level for an additional hour until substantially all the water was removed. The salt complex obtained is a liquid, brown in color, and did not contain any odor. The following properties were determined:

Basic No.	82.5
Percent sulfate ash	26.0
Metal ratio	4.2

EXAMPLE 58

6623 grams of the product produced in accordance with Example 57 were treated with SO_2 at 25–50° C. until 327 grams of the gas were combined with the salt complex. The product thus obtained had a neutralization number or a basic number of 0. The SO_2-salt complex product was liquid, brown in color, and did not contain any odor.

An experiment was conducted in order to determine whether air, which contains CO_2, would be effective as an acidic material. The examples below illustrate the utility of air for this purpose.

EXAMPLE 59

380 lbs. of a 30% solution of barium petroleum sulphonate having a 7.6% sulfate ash, 21.9 lbs. of para-tertiary-butyl phenol and 184 lbs. of water were combined and heated to 51° C. 68 lbs. of BaO were then added, and the temperature varied from about 51° C. to 64° C. over a period of about 1½ hours. The temperature was then raised to 100° C. and held there for 1 hour. Then the temperature was raised to 153° C. over about 4½ hours and held at that level for 1 hour. The complex was obtained by filtration and was found to have the following analysis:

Basic No.	80.5
Percent sulfate ash	26.0
Metal ratio	4.2

EXAMPLE 60

6000 grams of the product obtained in the above example, No. 59, were heated to 175° C. and blown with air for a period of about 13½ hours. The final product contained a basic no. of 1.1 and analyzed a 26.4% sulfate ash. It can be seen therefore that air can also be classified as an acidic material, because it lowered the basic no. and did not significantly change the metal content.

In all of the above examples the mahogany soap is referred to as barium petroleum sulphonate, and likewise the mahogany acid is similarly designated as petroleum sulphonic acid.

The oil-soluble barium sulphonates and/or oil-soluble sulphonic acids

The oil soluble barium sulphonates and/or sulphonic acids can be of the cyclic or aliphatic types. The cyclic compounds include the mono or polynuclear aromatic or cycloaliphatic compounds.

The oil soluble compounds can be represented by the following formulae:

I $[R_x\text{—}T\text{—}(SO_3)_y]_zM_b$

II $[R'\text{—}(SO_3)_a]_dM_b$

In the above formulae, M is either barium or hydrogen; T is a cyclic nucleus such as for example benzene, naphthalene, anthracene, phenanthrene, diphenylene, thioanthrene, phenothioxine, diphenylene sulphide, diphenylene oxide, diphenyl oxide, diphenyl sulphide, diphenyl amine, cyclohexane, petroleum naphthenes, decahydronaphthalene, cyclopentane, etc.; R is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, carboalkoxy-alkyl, etc. groups; x is at least one, and R_x contains a total of at least about 15–18 carbon atoms. R' in Formula II is an aliphatic radical containing at least about 15–18 carbon atoms and M is either barium or hydrogen. Examples of types of the R' radical are alkyl, alkenyl, alkoxyalkyl, carboalkoxyalkyl, etc. Specific examples of R' are petrolatum, saturated and unsaturated paraffin wax, polyolefins including poly C_3, C_4, C_5, C_6, C_7, C_8, etc. olefin hydrocarbons.

The groups T, R, and R' in the above formulae can also contain other organic or inorganic sub-

stituents in addition to those enumerated above, such as for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, carboxy, ester, ether, etc.

In Formula I, *x*, *y*, *z* and *b* are at least one, and likewise in Formula II, *a*, *b*, and *d* are at least one.

The following are specific examples of oil-soluble sulphonic acids coming within Formulae I and II above, and it is to be understood that such examples serve to also illustrate the barium salts of the sulphonic acids. In other words, for every sulphonic acid enumerated, it is intended that the barium salt thereof is also illustrated.

Such sulphonic acids are mahogany sulphonic acids; petrolatum sulphonic acids; mono- and polywax substituted sulphonic and polysulphonic acids of e. g.: naphthalene, phenol, diphenyl ether, naphthalene disulphide, diphenyl amine, thiophene, alpha-chloro-naphthalene, etc.; other substituted sulphonic acids such as cetyl-chlorobenzene sulphonic acids, cetyl-phenol mono-sulfide sulphonic acids, cetoxy capryl-benzene sulphonic acids, dicetyl-thianthrene disulphonic acid, di-lauryl beta-naphthol sulphonic acids, di-capryl nitro-naphthalene sulphonic acids; aliphatic sulphonic acids such as paraffin wax sulphonic acids, unsaturated paraffin wax sulphonic acids, hydroxy substituted paraffin wax sulphonic acids, tetraisobutylene sulphonic acids, tetraamylene sulphonic acids, chloro substituted paraffin wax sulphonic acids, nitroso paraffin wax sulphonic acids, etc.; cyclo-aliphatic sulphonic acids, such as petroleum naphthene sulphonic acids, cetyl-cyclopentyl sulphonic acids, lauryl-cyclohexyl sulphonic acids, bis (diisobutyl) cyclohexyl sulphonic acids, mono- or polywax substituted cyclohexyl sulphonic acids, etc. Additional examples of oil soluble sulphonic acids and/or barium salts thereof which can be used as starting materials are disclosed in the following U. S. patents: 2,174,110; 2,174,506; 2,174,508; 2,193,824; 2,197,800; 2,202,791; 2,212,786; 2,213,360; 2,228,598; 2,233,676; 2,239,974; 2,263,312; 2,276,090; 2,276,097; 2,315,514; 2,319,121; 2,321,022; 2,333,568; 2,333,788; 2,335,259; 2,337,552; 2,346,568; 2,366,027; 2,374,193; and 2,383,319.

With respect to the sulphonic acids or barium salts thereof, it is intended herein to employ the terms "petroleum sulphonic acids or barium petroleum sulphonates" to cover all such acids or salts derived from petroleum.

However, it is to be understood that all the sulphonic acids and barium salts enumerated above are not equivalent in their ability to complex with unusual amounts of barium inorganic compounds, because under certain conditions, some are more effective or desirable than others.

The promoter

The promoter employed in the process of this invention can be the organic compound AH wherein H is hydrogen and A is an anionic organic radical and/or the barium salt thereof. More particularly, the organic compound AXH is employed, wherein A and H are defined as given above for the compound AH and X is oxygen or sulfur. Also, the barium salt of AXH can be used alone or in admixture with the compound AXH. The compounds AH or AXH should have ionization constants measured in water at 25° C. greater than about 1×10^{-10}, water solubilities of at least about .0005% of 50° C. and saturated aqueous solutions of which exhibit a pH not greater than seven.

Generally, it is found that phenolic compounds, ionizable organic nitro compounds, e. g. nitroparaffins, lower molecular weight aromatic carboxylic acids, lower molecular weight organic thiophosphoric acids, the lower molecular weight sulphonic acids, hydroxy aromatic compounds, lower molecular weight hydroxy aromatic acids, etc., are suitable for the purposes of the present invention.

For the purpose of this specification and the appended claims, it should be understood that the "phenolic compounds" includes those compounds in which a hydroxyl group is directly attached to a benzenoid carbon atom, and which compounds may or may not contain other substituent groups. "A phenol" is referred to hereinafter as a subclass of phenolic compounds in which a single hydroxyl group is directly attached to a benzenoid carbon atom, and which compound may or may not contain a hydrocarbon group or plurality thereof in addition to said hydroxyl group. To better illustrate the wide variety of classes of compounds which can be employed in forming a salt complex in accordance with the present invention, specific examples are enumerated below. It is to be understood that while only the organic compounds AH are illustrated, it is intended that the barium salts thereof are included as specific examples.

The promoters found useful as promoters are phenol; alkylated phenols such as, for example, cresol, xylenol, p-ethyl phenol, di-ethyl phenols, n-propyl phenols, di-isopropyl phenols, p-t-butyl phenol, p-t-amyl phenol, p-cyclopentyl phenol, sec-hexyl phenols, n-heptyl phenols, diisobutyl phenols, 3,5,5-trimethyl-n-hexyl phenols, n-decyl phenols, cetyl phenols, etc.; aryl substituted phenols, e. g. phenyl phenol, diphenyl phenol, etc.; polyhydroxy aromatic compounds such as alizarin, quinezarin or polyhydroxy benzenes, e. g., hydroquinone, catechol, pyrogallol, etc.; monohydroxy naphthalenes, e. g. α-naphthol, β-naphthol, etc.; polyhydroxy naphthalenes, e. g., naphthohydroquinone, naphthoresorcinol, etc.; the alkylated polyhydroxy aromatic compounds such as octyl catechols, mono-(triisobutyl) pyrogallols, etc.; substituted phenols such as p-nitro phenol, picric acid, o-chlorophenol, t-butyl chlorophenols, p-nitro-o-chlorophenol, p-amino phenol, etc.; lower molecular weight hydroxy aromatic carboxylic acids such as salicylic acid, chloro-salicylic acids, di-isopropyl salicylic acids, gallic acid, 4-hydroxy-1-naphthoic acid, etc.; lower molecular weight aromatic sulphonic acids such as p-cresol sulphonic acid, p-t-butyl phenol sulphonic acid, beta-naphthol alpha-sulphonic acid, etc.; lower molecular weight aromatic acids such as benzoic acid, p-nitro benzoic acid, o-chloro benzoic acid, p-toluic acid, p-t-butyl benzoic acid, alpha naphthoic acid, etc.; lower molecular weight aromatic sulphonic acids such as benzene sulphonic acid, p-chlorobenzene sulphonic acid, p-nitrobenzene sulphonic acid, p-tolyl sulphonic acid, p-t-butyl benzene sulphonic acid, t-amyl-naphthalene sulphonic acids, etc.; lower molecular weight aliphatic sulphonic acids such as ethyl sulphonic acid, beta-chloro ethyl sulphonic acid, gamma nitro propyl sulphonic acid, octyl sulphonic acids, chloro-diisobutyl sulphonic acids, etc.; nitroparaffins such as 1-nitro propane, 2-nitro-n-butane, 1-nitro-1-(p-diisobutylphenoxy) propane, nitro paraffin wax, etc.; lower molecular weight thiophosphoric acids, e. g., tolyl monothiophosphoric acids, isopropyl-

phenyl monothiophosphoric acid, diisopropyl dithiophosphoric acids, etc.

Additional examples of lower molecular weight sulphonic acids and/or corresponding barium salts which can be used as promoters are disclosed in the following U. S. patents: 2,174,110; 2,174,111; 2,174,492; 2,174,505; 2,174,506; 2,174,507; 2,174,508; 2,174,509; 2,202,791; 2,228,598; 2,265,163; 2,276,097; 2,319,121; 2,321,022; 2,333,788; 2,335,259 and 2,337,552.

However, it is to be understood that the above-enumerated promoters are not equivalent, but that under certain conditions some are more effective than others.

Inorganic barium compounds

The salt complexes of the present invention are formed with an inorganic barium compound wherein the anionic radical, may be for example, hydroxyl, oxide, carbonate, bicarbonate, sulphide, sulfite, hydrosulphide, halide, hydride, amide, basic carbonate, etc. Of the inorganic barium compounds, good results are obtained with those having a water solubility of at least about 0.0003% at 50° C., and preferably at least about 0.006%. In a preferred instance, excellent results are obtained with the inorganic compounds of the basic type, that is, those compounds which in saturated aqueous solutions give an alkaline reaction, i. e. which have a pH value greater than 7.

To further illustrate the large number and variety of classes of inorganic barium compounds which can be employed, specific examples thereof are enumerated below.

The inorganic barium compounds include for example barium oxide, barium hydroxide, barium sulfide, barium carbonate, barium bicarbonate, barium hydride, barium amide, barium chloride, barium bromide, barium nitrate, barium sulfite, barium hydrosulfide, barium borate, etc. The corresponding basic salts of the just enumerated compounds are also intended.

Acidic material

As previously indicated, one form of the process of the present invention includes the step of treating the immediate product with an acidic material, which is defined herein as a material which possesses acidic characteristics when present in the mass containing the complex. This treatment effects the liberation of at least a portion of the material previously referred to as the promotor. A particularly effective acidic material which has been utilized for this purpose is carbon dioxide. We are aware of the fact that Mertes in his Patent No. 2,501,731 suggested transforming a sodium hydroxide-calcium sulphonate complex into the sodium carbonate-calcium sulphonate complex or the corresponding bicarbonate complex by blowing the hydroxide complex with carbon dioxide at elevated temperatures.

In our process, the step of treating with an acidic material such as CO_2 or air has the effect of liberating from the immediate complex product formed at least a portion of the promoter used. Thus the presence in the immediate complex product of the promoter material, in combined form, clearly distinguishes the immediate product from any organic metal complex type material heretofore produced. Moreover, the nature of the product formed by regenerating from the immediate product at least a portion of the promoter material leaves that product with a composition which is quite different from the other prior art organic metal complexes previously produced. It is recognized that in accordance with the present invention, the promoter in the form of a barium salt can be used; however, notwithstanding, upon treating the complex with an acidic material, the salt used as a promoter is freed from association in the complex as the metal-free promoter and not the barium salt.

For the purpose, that is, of releasing the promoter from the complex, an important feature or characteristic of the acidic material is that it must, when present in the mass containing the complex, possess an ionization constant greater then the organic compound used as the promoter. Thus for the purpose of this specification and the appended claims, it is to be understood that the acidic material can be either a liquid, gas or solid prior to being incorporated in the mass which contains the salt complex.

The acidic material usually employed is a liquid or a gas. The liquids can include the strong or weak acids, such as for example hydrochloric, sulphuric, nitric, carbonic acid, etc.; where as the gas is for the most part an anhydride of an acid or an "acid anhydride gas."

The following are additional specific examples of acidic materials, viz.: HCl, SO_2, SO_3, CO_2, air (considered acidic because of CO_2 content), NO_2, H_2S, N_2O_3, PCl_3, $SOCl_2$, ClO_2, H_2Se, BF_3, CS_2, COS, etc.

It is to be understood, however, that all the acidic materials are not equivalent, but that under certain conditions, some are more effective or desirable than others.

Process conditions

The salt complex of the present invention is prepared by combining the aforementioned compounds in the presence of water. The water can be present as a result of addition thereof to the mixture, or liberated from either the essential components or other additionally present compounds, as a result of being subjected to heat. However, it is preferred to add water to the mixture to effect salt complex formation. It has been found that the metal complex can be prepared when using small quantities of water, such as about 1 mole of water per mole of inorganic barium compound. However, more usually about 5 to 50 moles of water per mole of inorganic barium compound are used, and preferably about 15 to 30 moles per mole.

Generally, the complex obtained from using the inorganic barium compound, the oil-soluble sulphonic acid and/or the barium salt thereof, and the promoter, is prepared by heating the components in the presence of water at a superatmospheric temperature while insuring thorough mixing, and then still further heating said mixture to substantially remove all of the water. At least five methods are available by which the complex can be formed, namely:

(*a*) The promoter is added to the oil-soluble normal salt of sulphonic acid, followed by an addition of an aqueous solution or suspension of the inorganic barium compound thereto, the mixture is held at a superatmospheric temperature for a reasonable length of time while effecting thorough mixing, and then the total mixture is further heated to remove substantially all the water;

(*b*) The inorganic barium compound in a dry state is added to a mixture of sulphonic acid or

normal sulphonate, promoter and water, heating while insuring thorough mixing and then further heating to remove substantially all of the water;

(c) The acid of the desired sulphonate is mixed with the promoter, then an aqueous solution or suspension of the inorganic barium compound is added thereto, the mixture is heated and agitated at a superatmospheric temperature for a time sufficient to insure thorough mixing and followed by subjecting the total mixture to dehydration conditions in order to remove substantially all of the water;

(d) In all of the methods described herein, the mixture containing the complex product is treated with an acidic material just prior to filtering, and then the desired complex is separated from other uncombined materials; and

(e) The sediment formed from any of the aforementioned methods can be employed either alone or with additional promoter in any of the three methods given above.

In all of the methods described above for preparing the salt complex, the step of removing substantially all of the water is accomplished at a temperature not substantially in excess of 350° C., preferably about 110° to 200° C. The technique employed to remove the water includes for example a conventional flash stripping operation, which involves passing the material in a thin film state over a large heated area of glass, ceramic or metal; heating under subatmospheric pressures; as well as heating under either atmospheric or superatmospheric pressure. It can therefore be seen that the temperature as well as the time for effecting substantial removal of water will vary considerably, depending on the technique employed therefor. Generally, the time required to effect substantial removal of water, when employing drying other than flash techniques, is about 15 minutes or less, and can be as high as 10–15 hours. Usually, however, it is most convenient to employ atmospheric pressure for such an operation, and consequently it requires about 1 to 5 hours to remove substantially all of the water. At a later stage of the process, the acidic material when used in gaseous form may be used to remove the last portion of water.

For the purposes of this specification and the appended claims, the relative chemical equivalents of oil soluble sulphonic acid and/or barium salt thereof and promoter is expressed as the "ratio of equivalents" of the former to the latter. In accordance therewith, the ratio of equivalents of oil soluble sulphonic acid and/or barium salt thereof to promoter is from about 1 to 10 to about 10 to 1, preferably from about 3 to 2 to about 7 to 2.

The amount of inorganic barium compound employed, generally, will be sufficient to have present in the total mass at least more than about one equivalent of barium regardless of how combined, per equivalent of oil soluble sulphonic acid and/or barium salt thereof plus promoter. In other words, the amount of inorganic barium compound employed must be such that there is more than enough to theoretically form merely a normal salt of oil soluble sulphonic acid and a barium salt of the promoter. Thus, for the purposes of this specification and the appended claims, the amount of inorganic barium compound employed will be expressed as in an amount such that there are present in the mass substantially more than one equivalent of barium, including the barium which is present in the form of the salt of the oil soluble sulphonic acid and/or the organic compound AH used as a promoter per equivalent of oil soluble sulphonic acid and/or barium salt thereof plus the promoter.

As mentioned above, the metal content of the complex can be significantly increased by treating the mixture with an acidic material prior to filtering same to recover the desired product or salt complex. In general, about 0.5 to 20% of the acidic material, based on the weight of the total mass, is employed at a temperature not substantially in excess of 350° C., more usually about 25 to 250° C., and preferably 50° to 170° C., and for a period of about 0.25 to 30 hours. The time of treatment varies considerably depending on the results desired and the type of acidic material employed. Treatment with an acidic anhydride gas may be accelerated by superatmospheric pressure.

As indicated hereinabove, treatment of the separated salt complex product with an acidic material is done in instances where it is desirable to lower the basic number of the salt complex and/or partially or substantially completely recover the promoter. This treatment is effected at a temperature of about 25° to 250° C., preferably about 50° to 170° C., and by usually employing about 0.5 to 20% of acidic material, based on the weight of salt complex. The time of treatment with the acidic material can vary considerably, depending on the desired result. As would be expected, short periods of treatment will cause only partial liberation or release of the promoter or small decreases in the basic number of the salt complex. However, in general, periods of treatment will range from about 0.25 to 30 hours.

In most cases, and particularly where it is desired to recover the promoter, the amount of acidic material used should be at least equivalent to the amount of metal present as the salt of the ionizable form of promoter.

When it is desired to produce a product having substantially neutral reaction, the amount of acidic material used should be at least equivalent to the total metal in excess of that present as the normal salt of the oil soluble organic acid.

As indicated above, in order to facilitate an understanding of the amount of metal which can be present in the salt complex, the "metal ratio" is defined as the ratio of the total metal in the salt complex to the amount of metal which is in the form of a normal salt of the oil-soluble sulphonic acid. In accordance therewith, the salt complex formed with the oil-soluble sulphonic acid and/or barium salt thereof, the promoter and the inorganic barium compound include metal ratios greater than 1 and up to about 10 or more. As for the complex which is treated with an acidic material, the metal content is substantially the same as in the complex prior to treating. Consequently, the same metal ratio as given above will apply to such treated products. In those instances where the salt complex is treated with an acidic material and the ionizable organic compound is removed from the resultant product by distillation or otherwise, it is found that the metal ratios will be substantially the same as in the salt complex before treating with the acidic material.

By reason of the high metal ratio of the complexes produced in accordance with this invention, the following theories are suggested as a possible explanation of how the metal is combined. It is to be understood, however, that such

theories are advanced for the purpose of offering explanations, and are not to be construed as limitations on the scope of the present invention.

In the following equations, AXH represents a promoter in which H is an ionizable hydrogen and M represents a divalent metal. Assuming that the promoter may act as a catalyzer for the formation of inorganic polymeric configurations, viz. $(—M—O—)_xH$, which are bonded to the acid group, (e. g. the sulphonate radical in the preferred instance), the possible reactions that may occur with the sulphonate radical are:

(1) $2RSO_3H + M(OH)_2 \longrightarrow (RSO_3)_2M + 2H_2O$

(2) $(RSO_3)_2M + M(OH)_2 \longrightarrow 2RSO_3M—OH$

(2a) $RSO_3M—OH + AXH \longrightarrow RSO_3M—XA + H_2O$

(3) $RSO_3M—OH + M(OH)_2 \xrightarrow[\text{Catalyst}]{AXH} RSO_3M—O—M—OH + H_2O$

(3a) $RSO_3M—O—M—OH + AXH \longrightarrow RSO_3M—O—M—XA + H_2O$

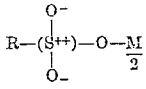
(4) $RSO_3—M—O—M—OH + M(OH)_2 \xrightarrow[\text{Catalyst}]{AXH} RSO_3—M—O—M—O—MOH + H_2O$

(4a) $RSO_3M—O—M—O—MOH + AXH \longrightarrow RSO_3M—O—M—O—MXA + H_2O$

(5) $2AXH + M(OH)_2 \longrightarrow (AX)_2M$ (peptized into end product).

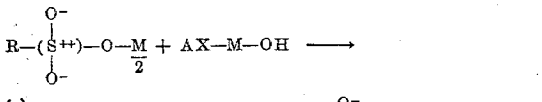
The resultant complex, according to the above theory, can be a complex mixture of all the potential products listed above. It is apparent that high metal ratios are possible under this theory.

Another theory is based upon an electronic interpretation. For example, in the case of the neutral sulphonate, the charges are distributed as follows:

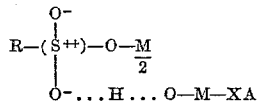


The electron octets around the two oxygen atoms which are not attached to a metal atom give to each of these atoms a unit negative charge, thus leaving the sulfur atom with a double positive charge.

When the sulphonate, excess inorganic metal compound, promoter and water are reacted according to the present invention, a basic promoter salt, AX—M—OH is presumed to be formed. This normally oil-insoluble salt dissolves in the reaction mixture because of the electronic attracting force known as a hydrogen bonding. Structurally this can be shown as:

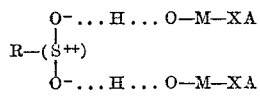


(a)



and

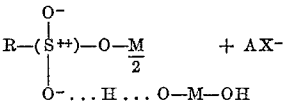
(b)



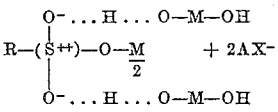
Structure (a) would have a metal ratio of 3.0, and structure (b) would have a metal ratio of 5.0. Combinations of neutral sulphonate and one or both structures would explain the whole number and fractions of metal ratios which are obtained in actual practice.

After the structure (a) and (b) are formed, if hydroxyl ions are present in the reaction mass the following reactions may take place:

Structure (a) + OH^- ⟶



Structure (b) + $2OH^-$ ⟶



The AX^- ions may then react with $M(OH)_2$ to produce more AX—M—OH, and the latter would in turn lead to the formation of additional amounts of structures (a) and (b). The cycle may occur repeatedly.

According to this electronic explanation, the AX^- residue of the basic promoter salt

AX—M—OH

appears to function as a carrier for the $M(OH)_2$, and thus facilitating the communicating of the $M(OH)_2$ into close positions with the negatively charged oxygen atoms of the sulphonate radical.

Having thus described the present invention by furnishing specific examples thereof, it is to be understood that no undue limitations or restrictions are to be imposed by reason thereof, but that the scope of this invention is defined by the appended claims.

The salt complexes produced in accordance with the present invention can be employed in lubricants including oils and greases, and for such purposes as in crankcases, transmissions, gears, etc., as well as in torque converter oils. Other suitable uses for such complexes are in asphalt emulsions, insecticidal compositions, fire-proofing agents in plasticizers and plastics, paint driers, rust inhibiting compositions, pesticides, foaming compositions, cutting oils, metal drawing compositions, flushing oils, textile treatment compositions, tanning compositions, metal cleaning compositions, emulsifying agents, antiseptic cleansing compositions, penetrating agents, gum solvent compositions, fat splitting agents, bonding agents for ceramics and asbestos, asphalt improving agents, flotation agents, improving agents for hydrocarbon fuels such as, e. g., gasoline and fuel oil, etc.

More particularly, the complexes of this invention are especially adapted for the preparation of lubricants, paint driers and plastics, especially the halogen bearing plastics. In these respects, the salt complex can be employed in the following concentrations based upon the weight of the total composition.

	Broad range	Usual range	Preferred range
	Percent	*Percent*	*Percent*
Lubricants	0.01–20	0.2–15	0.5–10
Stabilizing agent for plastics	0.05– 5	0.1– 3	0.2– 2
Paint Drier	0.2 –25	0.5–20	1.0–15

To better appreciate the wide variety of uses to which the salt complexes of this invention are adapted, the following specific examples are given:

Use in a lubricant:	Per cent by weight
SAE 30 motor oil	96.0
Product of Example 36	3.0
P_2S_5 treated turpentine	0.25
Barium di-lauryl dithiophosphate	0.75

Use as a stabilizing agent for halogen-bearing plastics:

Poly-vinyl chloride	70.0
Di-octyl phthalate	28.75
Product of Example 14	1.25

Use as a paint drier:

Titanium-base house paint	97.0
Product of Example 19	3.0

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such be employed.

We therefore particularly point out and distinctly claim as our invention:

1. A process which comprises preparing and mixing a mass in which, at 50° C., at least 50% of the components are in the liquid state, and in which mass the active components consist of:

A. An organic compound selected from the class consisting of oil-soluble organic sulphonic acid compounds having a total of at least 18 carbon atoms and the barium salts thereof;

B. An organic compound selected from the class consisting of phenolic organic compounds and the barium salts thereof, said organic compound having:

(a) An ionization constant in water of at least about 1×10^{-10} at about 25° C.;

(b) A water solubility at 50° C. of at least about 0.0005%; and

(c) In saturated aqueous solutions at about 25° C. a pH of less than 7;

the relative amounts of A and B used being in the range of from about one equivalent of A to about 10 equivalents of B to about 10 equivalents of A to about one equivalent of B;

C. An inorganic barium compound;

(1) Which is water-soluble at a temperature of 50° C. to the extent of at least about 0.0003%;

(2) In an amount such that there are present in the mass substantially more than 1 equivalent of barium, including the barium present in the remaining components, per equivalent of A plus B; and

D. Water, in an amount equal to at least about one mole per mole of C;

maintaining the mass at a temperature and for a period of time sufficient to drive off substantially all free water and water of hydration which may be present, and form the organic barium complex; and then treating the organic barium complex with carbon dioxide in amounts sufficient to liberate a substantial proportion of said organic compound of component B.

2. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble organic sulphonic acid.

3. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble cyclic sulphonic acid.

4. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble aromatic sulphonic acid.

5. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble aliphatic substituted single ring aromatic sulphonic acid.

6. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble alkyl substituted benzene ring sulphonic acid containing at least 15 alkyl carbon atoms.

7. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble hydroxy substituted single ring aromatic sulphonic acid.

8. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble wax phenol sulphonic acid.

9. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble cycloaliphatic sulphonic acid.

10. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble mahogany acid.

11. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble aliphatic sulphonic acid.

12. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble straight-chain acyclic sulphonic acid.

13. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble chlorinated paraffin wax sulphonic acid.

14. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble branched chain acyclic sulphonic acid.

15. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound which is component A is an oil-soluble chlor-White oil sulphonic acid.

16. A process in accordance with claim 1 characterized further in that the organic compound which is component B is a phenolic organic compound.

17. A process in accordance with claim 1 characterized further in that the organic compound which is component B is phenol.

18. A process in accordance with claim 1 characterized further in that the organic compound which is component B is a not more than 16 carbon hydrocarbon substituted phenolic organic compound.

19. A process in accordance with claim 1 characterized further in that the organic compound which is component B is a lower alkyl substituted phenolic organic compound.

20. A process in accordance with claim 1 characterized further in that the organic compound which is component B is diisobutyl phenol.

21. A process in accordance with claim 1 characterized further in that the organic compound which is component B is tertiary butyl phenol.

22. A process in accordance with claim 1 characterized further in that the organic compound which is component B is a barium salt of a phenolic organic compound.

23. A process in accordance with claim 1 characterized further in that the organic compound which is component B is a barium salt of a not more than 16 carbon hydrocarbon substituted phenolic organic compound.

24. A process in accordance with claim 1 characterized further in that the organic compound which is component B is a barium salt of a lower alkyl substituted phenolic organic compound.

25. A process in accordance with claim 1 characterized further in that the organic compound which is component B is the barium salt of diisobutyl phenol.

26. A process in accordance with claim 1 characterized further in that the organic compound of component B is a non-metal inorganic substituted phenol.

27. A process in accordance with claim 1 characterized further in that the organic compound of component B is tertiary-butyl chloro phenol.

28. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound of component A is petroleum naphthene sulphonic acid.

29. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound of component A is a wax phenol sulphonic acid, and the organic compound of component B is phenol.

30. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound of component A is mahogany acid, and the organic compound of component B is diisobutyl phenol.

31. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound of component A is chlorinated paraffin wax sulphonic acid, and the organic compound of component B is tertiary butyl phenol.

32. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound of component A is chlor-White oil sulphonic acid, and the organic compound of component B is the barium salt of diisobutyl phenol.

33. A process in accordance with claim 1 characterized further in that the organic sulphonic acid compound of component A is petroleum naphthene sulphonic acid, and the organic compound of component B is tertiary butyl chloro phenol.

34. As a new composition of matter, an oil-soluble reaction product produced by the process of claim 1, which is substantially free of a salt of said low molecular weight organic compound of component B.

35. As a new composition, the oil-soluble reaction product mass produced by the process of claim 1, which includes as a component thereof a substantial proportion of the metal-free, low molecular weight organic salt-forming compound of component B liberated from said organic alkaline-earth metal complex.

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