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ORGANIC ALKALINE EARTH METAL COMPLEXES AND METHOD OF MAKING SAME

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This invention relates to organic metal complexes and novel methods for the production of such complexes.

It is now well known that when preparing a salt or soap of an organic acid, the mere use of an excess of neutralizing agent, which in the prior art has been in the form of the oxide, hydroxide, carbonate, etc. of the desired metal, may result in a product which contains an amount of metal in excess of that theoretically required to replace the acidic hydrogens of the organic acid used as the starting material.

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 these so-called basic salts or soaps.

Among the earlier workers in the art who recognized this factor and indicated that the use of basic soaps 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 soap without, however, giving any specific method for the preparation of such soaps. A similar disclosure is found in Van Ess Patent No. 2,372,411.

With the demonstrated superiority of such basic 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 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 neutralizing agent was employed in a process more or less conventional for producing salts or soaps excepting that the process was carried out in the presence of steam in order 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

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disclosure on the hypothesis 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. 2,501,731 was granted March 28, 1950. Mertes first prepared the normal soap 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." The disclosure in Mertes appears to indicate 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 alkaline earth metal which can be held in combination or in colloidal suspension by means of these prior art processes. The greatest total amount of alkaline earth metal which can possibly be thus incorporated in the product by means of any of these prior art processes has been obtained when using barium and in that case it is 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 organic acid will hereinafter be referred to as the "metal ratio."

By means of the present invention, it is now possible to obtain alkaline earth metal 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 concentration 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 alkaline earth metal organic complexes are produced in accordance with the present invention as a fluid,

which is readily adapted for application where high concentrations of alkaline earth metal 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 our invention to provide an alkaline earth metal organic complex which contains in stable form an amount of metal substantially greater than that contained in any of the so-called alkaline earth metal complexes previously produced. It has been found that a metal ratio substantially greater than that possible with the prior art processes give 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 alkaline earth metal as in complexes produced by the prior art process 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 alkaline earth metal complexes.

Further objects of our 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 a salt-forming material with an organic acid compound (to be understood hereinafter as the acid itself and/or an alkaline earth metal 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 in the inorganic metal compound, whereas among 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 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 end product is, similar to the initial product, of utility as a lubricant additive.

Stated more particularly, the present invention comprises the improvement in the process of producing an alkaline earth metal complex of oil-soluble organic acids, wherein an organic acid compound (to be understood hereinafter as the acid itself and/or an alkaline earth metal salt thereof) is caused to combine with a salt-forming metal compound under conditions which would produce a normal salt, which comprises increasing the amount of metal which will be thus combined by having present in the process mass.

- (a) An amount of such metal compound substantially in excess of the stoichiometric amount required to form the normal metal salt;
- (b) An organic compound selected from the class consisting of those organic compounds which are water-soluble at a temperature of 50° C. to the extent of at least 0.0005% and which in the presence of water have an ionization constant greater than about 1×10^{-10} at about 25° C.; and the salts of such organic compounds; and
- (c) Water, including free and combined water in the other components;

and 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.

A more specific aspect of the process comprising this invention may be defined as the process of producing an alkaline earth metal organic complex which comprises:

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

- A. An oil soluble organic acid compound;
- B. An organic compound containing an element of group VI of the periodic chart which has an atomic number less than 17, which compound is selected from the class consisting of:

- (1) An organic compound AH in which H is hydrogen and A is an organic anionic radical, 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 not greater than about 7;

- (2) The alkaline earth metal 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 one equivalent of B;

- C. An inorganic alkaline earth metal compound

- (1) Which is water-soluble at a temperature of 50° C. of at least 0.003%
- (2) In an amount such that there are present in the mass substantially more than 1 equivalent of alkaline earth metal, including the alkaline earth metal 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,

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.

In the above-outlined processes, following Step II, the mass or product can be optionally treated in accordance with Steps III and IV given below.

III. Then treating the mass or product with a material which in the presence of the mass or product will form a material having a higher ionization constant than the promoter, and optionally;

IV. Removing from the mass or product so much of the liberated or released promoter as may have been formed 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 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 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 alkaline earth 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, CO₂, and 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 I

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 1.74) 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
Per cent 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	...do....	...do....	Do....
Do.....	1	...do....	...do....	Do....

The above preparation, which is an example of

the present invention, is compared with a basic sulphonate prepared in accordance with a conventional technique and which is described below.

EXAMPLE 2

500 grams of the barium salt of the petrolatum sulphonic acid given in Example 1 were 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 was filtered. The resultant basic sulphonate has the following properties:

Basic No. _____ 5.27
Per cent sulphate ash _____ 9.85
Metal ratio _____ 1.08

EXAMPLE 3

1000 grams of the barium salt of unsaturated paraffin wax sulphonic acid containing 13.1% sulphate 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 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 by filtration. The salt complex thus prepared had the following properties:

Basic No. _____ 53.8
Per cent sulphate 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	...do....	...do....	Do....
Do.....	1	...do....	...do....	Do....

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 filtered with the aid of Hyflo in order to separate the complex salt. The salt complex had the following properties:

Basic No. _____ 16.2
Per cent sulphate 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% sulphate 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 the reflux temperature, and then dehydrated at about 165° C. for a period of one hour. Hyflo was then added to the product and the salt complex was recovered by filtration. The salt complex contained the following properties:

Basic No.	44.1
Per cent sulphate 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 (113 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 filtration. 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
Per cent sulphate 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% sulphate ash and 27 grams of para-tertiary-butyl phenol were placed in a suitable vessel and heated to 90° C. (ratio of equivalents is 1.54). 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 product was a viscous liquid, black in color, and contained a very slight odor. The following properties were determined for the salt complex:

Basic No.	69.7
Per cent sulphate 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
Per cent sulphate 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 sulphate ash 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 organic acids or salts thereof were combined in accordance with the method of the present invention. In the following examples, 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 in a 12-liter, 3-neck flask (ratio of equivalents 1.7) 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 there 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 a 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
Per cent sulphate ash	23.1
Metal ratio	3.59

EXAMPLE 10

405 grams of di-(2-ethyl hexyl) dithiophosphoric acid, 99 grams of para-tertiary-butyl phenol (ratio of equivalents 1.52) and 473 grams of solvent extracted Mid-Continent oil having a viscosity of 160 SUS @ 100° F. were mixed together and heated to 50° C. A slurry comprising 387 grams of BaO and 1,030 cc. of water was added quickly, maintaining the temperature at about 65° C. The mixture was then heated to 100° C. and held there for one hour. Then the temperature was raised to 150° C. over a period of 2½ hours and held there for one hour. The product was obtained by filtering the mass and was found to be a slightly viscous liquid, red in color, and contained a slight odor. The following properties were determined for the product:

Basic No.	76.0
Per cent barium	20.0
Per cent sulphate ash	34.0
(calculated from metal content)	
Metal ratio	3.65

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EXAMPLE 11

620 grams of di-(2-ethyl-hexyl) mono-thio-phosphoric acid, 310 grams of isononyl phenol (ratio of equivalents is 1.52), 755 grams of mineral oil having 160 SUS @ 100° F. and 2060 ml. of water were mixed together. Then 774 grams of BaO were added over a half hour period. The total mixture was then refluxed for one hour at 100° C. whereupon the temperature was raised to 150° C. and held at that level for one hour. The temperature of the mixture was allowed to cool to 50–60° C. and then blown with CO₂ to obtain a neutral product. The complex obtained had the following properties:

Acid No.	6.85
Per cent barium	17.2
Metal ratio	2.65

EXAMPLE 12

777 grams of di-(2-ethyl hexyl)dithiophosphoric acid, 308 grams of iso-nonyl phenol (ratio of equivalents 1.52) and 914 grams of solvent extracted Mid-Continent oil having a viscosity of 160 SUS @ 100° F. were mixed together, followed by an addition of BaO slurry consisting of 773 grams of BaO and 2,060 cc. of H₂O, while keeping the temperature below 65° C. The total mixture was then heated at 100° C. for one hour, followed by a raise in temperature to 150° C. over a period of 2½ hours, and maintained at that level for one hour. The desired product was a slightly viscous liquid, red in color, and contained a slight odor. The product had the following properties:

Basic No.	78.0
Per cent barium	22.7
Per cent sulphate ash	38.6
(calculated from metal content)	
Metal ratio	4.52

EXAMPLE 13

172 grams of di-(n-hexyl)dithiophosphoric acid, 500 grams of petroleum sulphonic acid, 159 grams of iso-nonyl phenol (ratio of equivalents of oil soluble acids to iso-nonyl phenol is 1.52), and 1,170 cc. of water were mixed together, then 437 grams of BaO were added over a period of ½ hour. The mixture was heated at reflux temperature for 1 hour, followed by heating to 150° C. over a period of 2½ hours, and then maintaining that temperature for 1 hour. The desired product was a viscous liquid, brown in color, and contained a slight odor. The following properties were determined:

Basic No.	87.1
Per cent barium	28.6
Per cent sulphate ash	48.8
(calculated from metal content)	
Metal ratio	5.22

EXAMPLE 14

172 grams of di-(n-hexyl)dithiophosphoric acid, 500 grams of petroleum sulphonic acid and 98 grams of para-tertiary-butyl phenol (ratio of equivalents of oil soluble acids to para-tertiary-butyl phenol is 1.52) were mixed together. To this mixture was added a slurry of 387 grams of BaO and 1,080 cc. of water. The mixture was heated at 100° C. for one hour, and then the temperature was raised to 150° C. and held at that level for one hour. The product was a highly viscous liquid, brown in color, and con-

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tained a slight odor. The following properties of the product were determined:

Basic No.	121
Per cent barium	30.05
Sulphate ash	51.0
(calculated from metal content)	
Metal ratio	5.36

EXAMPLE 15

249 grams of petroleum naphthenic acid, 88.6 grams of para-tertiary butyl phenol (ratio of equivalents is 1.70), 1212 grams of a conventionally-refined Mid-Continent oil having a viscosity of 110 SUS @ 100° F., 347 grams of BaO, and 700 ml. of H₂O were placed in a 5 liter, 3 neck flask and heated to 100° C. with stirring. The mixture was held at 100–105° C. for 1 hour, and then the temperature was raised to 150–160° C. After holding the temperature for 1 hour at 150–160° C., the mixture was blown with CO₂ for ¾ hour, keeping the temperature at about 150–160° C. The mixture was then filtered with Hyflo, and the separated product had the following properties.

Basic No.	1.98
Per cent sulphate ash	25.10
Metal ratio	4.10

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 16 and 17 below.

EXAMPLE 16

A mixture containing 500 grams of the barium salt of petrolatum sulphonic acid (sulphate ash 9.2%) 197 grams of the barium salt of petroleum sulphonic acid (sulphate ash 7.6%), and 50 grams of para-tertiary-butyl phenol (ratio of equivalents of the sulphonates to promoter 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
Per cent sulphate ash	17.25
Metal ratio	2.41

EXAMPLE 17

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 16 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 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.	20.2
Per cent sulphate ash	11.72
Metal ratio	1.51

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 complex, nevertheless it is contemplated for the purposes of this invention to employ the complexes produced by conventional techniques as a starting material. The following example illustrates this concept:

EXAMPLE 18

1634 grams of a barium petroleum sulphonate-BaO complex (obtained by dehydrating a barium petroleum sulphonate, 7.6% sulphate 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% sulphate ash) and 121 grams of di-isobutylphenol (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 three hour period and held there for one hour. Prior to filtering, the mass was blown with CO₂ at a rate of 3.6 cubic foot/hr. for 1½ hours at 150° C. The product analyzed as follows:

Basic No.	8.67
Per cent sulphate ash	24.8
Metal ratio	4.13

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

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 19 and 20 below illustrate the effect of higher temperatures.

EXAMPLE 19

2000 grams of a 30% oil solution of barium petroleum sulphonate (sulphate ash 7.6%) were mixed with 120 grams of paratertiary-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
Per cent sulphate ash	24.3
Metal ratio	3.80

EXAMPLE 20

2036 grams of 30% oil solution of barium petroleum sulphonate (sulphate 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 tem-

perature 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
Per cent sulphate ash	32.8
Metal ratio	5.56

In addition to the promoters tested above, various other promoters were tried to determine the effectiveness thereof in preparing the complexes of the present invention.

EXAMPLE 21

A mixture of 2280 grams of 30% oil solution of barium petroleum sulphonate (sulphate 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 one-half hour. The resultant salt complex was fluid in consistency and dark red in color. The following properties were determined:

Basic No.	91.4
Per cent sulphate ash	26.8
Metal ratio	4.37

EXAMPLE 22

The ionizable organic compound or promoter employed in this test was prepared by reacting 80 grams 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 sulphonc 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 sulfonic acid is 1.52). The mixture was heated to 90° C., whereupon 284 grams of barium oxide and 760 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
Per cent sulphate ash	27.0
Metal ratio	4.73

EXAMPLE 23

2500 grams of 30% oil solution of barium petroleum sulphonate (sulphate 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
Per cent sulphate ash	19.1
Metal ratio	2.88

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EXAMPLE 24

630 grams of a 30% oil solution of barium petroleum sulphonate (7.6% sulphate ash) were admixed with 350 grams of nitro-paraffin 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
Per cent sulphate ash	33.3
Metal ratio	6.47

EXAMPLE 25

2050 grams of a 30% oil solution of barium petroleum sulphonate (sulphate 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 an oily liquid, reddish-brown in color, and contained a slight odor. The following properties were determined for the product:

Basic No.	78.2
Per cent sulphate ash	28.2
Metal ratio	4.60

EXAMPLE 26

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 two hour period, where the temperature was held for one-half hour. The total mixture was filtered, and the filtered product had the following properties:

Basic No.	87.8
Per cent sulphate ash	25.95
Metal ratio	3.88

EXAMPLE 27

1140 grams of a 30% oil solution of barium petroleum sulphonate having a sulphate ash of 7.6% and 80 grams of para-tertiary-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
Per cent sulphate ash	24.60
Metal ratio	3.96

EXAMPLE 28

2583 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash, 144.2 grams of beta-naphthol (ratio of

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equivalents is 1.69) and 1262 ml. of water were combined and mixed thoroughly. Then 472 grams of BaO were added over a one hour period, followed by maintaining the total mixture at 100° C. for one hour. The temperature was then raised to 150° C. and held there for one hour. Prior to filtering the mixture, it was blown with CO₂ 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
Per cent sulphate ash	23.8
Metal ratio	3.90

EXAMPLE 29

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate 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 one hour. The temperature was then raised to 150–160° C. and held there for one hour. Prior to filtering, the mass was blown at about 150° C. with CO₂ until a basic number of about 1 was obtained. The filtered product analyzed as follows:

Basic No.	3.9
Per cent sulphate ash	25.0
Metal ratio	4.17

EXAMPLE 30

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate 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 one hour. Then the temperature was raised to 150° C. where it was held for one hour. Prior to filtering the mixture, it was blown for three hours with CO₂ at 135–145° C. until the mixture was slightly basic. The filtered product analyzed as follows:

Basic No.	13.3
Per cent sulphate ash	25.45
Metal ratio	4.38

EXAMPLE 31

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate 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 one hour, then heated to 150° C. over a three hour period and held there for one hour. Prior to filtering, the mixture was blown with CO₂ at 150° C. and at a rate of 3.6 cu. ft./hr. for one and one-half hours. The filtered product analyzed as follows:

Acid No.	0.45
Per cent sulphate ash	24.7
Metal ratio	4.34

EXAMPLE 32

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate 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 H₂O, followed by a slow

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addition of 271 grams of BaO. Then entire mixture was then refluxed for one hour, and then heated to 150° C. over a three hour period. The mixture was held at 150° C. for one hour. Prior to filtering, the mass was blown at 150° C. with CO₂ at a rate of 3.6 cu. ft./hr. for 1½ hours. The filtered product analyzed as follows:

Acid No.	0.41	
Per cent sulphate ash.....	24.1	10
Metal ratio	4.12	

EXAMPLE 33

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash and 131 grams of methyl naphthalene sulphonic 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 one 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 CO₂ at a rate of 3.6 cu. ft./hr. for 1½ hours at 150° C. The filtered product analyzed as follows:

Basic No.	Nil	
Per cent sulphate ash.....	25.9	
Metal ratio	4.41	

EXAMPLE 34

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash, 113 grams of diisobutenyl sulphonic acid (ratio of equivalents is 1.7) and 725 grams of H₂O were combined and heated to 700° C. To this mixture were added 271 grams of BaO, and the entire mixture was heated at 100° C. for one hour. The mixture was then heated at 150° C. for one hour, followed by blowing with CO₂ at 150° C. prior to filtering, to obtain a substantially neutral mass. The filtered product analyzed as follows:

Basic No.	0.23	
Per cent sulphate ash.....	24.6	
Metal ratio	4.10	

EXAMPLE 35

Di-isopropyl benzene sulphonic acid obtained by reacting 162 grams of di-isopropyl benzene with 122 grams of chloro sulphonic acid for one hour at 100° C. were combined with 2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate 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 one hour. The temperature was raised to 150° C. and held there for one hour. Prior to filtering, the mixture was blown with CO₂ for one half hour at 120-140° C. The filtered product analyzed as follows:

Acid No.	1.22	
Per cent sulphate ash.....	25.4	
Metal ratio	4.33	65

EXAMPLE 36

Cymene sulphonic acid obtained by reacting 134 grams of cymene with 122 grams of chloro-sulphonic acid at 70-100° C. for 1½ hours were combined with 2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash and 1220 ml. of water. The ratio of equivalents of oil soluble sulphonate to sulphonic acid is 1.7. To this mixture were added

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461 grams of BaO, and the entire mixture was then held at 85-100° C. for one hour. Then the temperature was raised to 150° C. and held there for one hour. Prior to filtering, the mass was blown with CO₂ for one-half hour at 130° C. The filtered product analyzed as follows:

Acid No.	0.95	
Per cent sulphate ash.....	25.8	
Metal ratio	4.38	

EXAMPLE 37

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate 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 one hour, followed by maintaining the temperature at 150° C. for one hour. Prior to filtering, the mass was blown with CO₂ for 90 minutes at 135-150° C. until it was slightly acidic. The filtered product analyzed as follows:

Basic No.	6.45	
Per cent sulphate ash	23.2	
Metal ratio	3.85	

EXAMPLE 38

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate 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 one hour, and then heated to 150° C. and held there for one hour. Prior to filtering, the mass was blown with CO₂ for 20 minutes at 125-150° C. The filtered product analyzed as follows:

Acid No.	0.27	
Per cent barium.....	14.25	
Per cent sulphate ash.....	24.2	
(calculated from metal content)		
Metal ratio	4.15	

EXAMPLE 39

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate 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 one hour period. The entire mixture was held at 94° C. for one hour, followed by a one hour period of heating at 150° C. Prior to filtering, the mass was blown with CO₂ for one hour at 135-150° C. The filtered product analyzed as follows:

Acid No.	0.2	
Per cent sulphate ash	22.8	
Metal ratio	3.48	

EXAMPLE 40

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate 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 one hour, and then held at 150° C. for one hour. Prior to filtering, the mixture was blown with CO₂ at a rate of 3.6 cu. ft./hr. for 1.25 hours at a tem-

perature of 150° C. The filtered product analyzed as follows:

Acid No.	0.24
Per cent sulphate ash	23.6
Metal ratio	4.12

The salt complex can also be prepared by starting with the oil-soluble sulphonic acid and treating with a 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 or conventionally overbased 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 with a conventional technique in which the acid was employed as a starting material. In this respect, Examples 41 and 42 below are illustrative.

EXAMPLE 41

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 reaction mixture to stand 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 para-tertiary-butyl phenol, (ratio of equivalents is 1.39), 1647 grams of a 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
Per cent sulphate ash	24.4
Metal ratio	4.02

EXAMPLE 42

500 grams of the oil-soluble petroleum sulphonate given in Example 41 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
Per cent sulphate ash	25.65
Metal ratio	1.74

The salt complexes of the present invention can be prepared by first adding water to the mixture of the oil-soluble metal sulphonate or sulphonate acid and promoter, and then adding the inorganic metal compound in a dry state. In this respect, Example 43 given below illustrates an alternative method by which the salt complex can be prepared.

EXAMPLE 43

1000 grams of the barium salt of di-paraffin wax substituted phenol sulphonate (sulphate 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 SUS at 100° F. The temperature was raised over a period of four hours to 170° C. and then maintained there 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 following properties were determined for the salt complex:

Basic No.	67.8
Per cent sulphate ash	23.8
Metal ratio	2.67

Another experiment was performed in which the salt of the ionizable organic compound was employed as the promoter. Example 44 below illustrates this feature of the invention.

EXAMPLE 44

1700 grams of a 30% oil solution of barium petroleum sulphonate (sulphate ash 7.6%) were admixed with 105 grams of barium phenate (ratio of equivalents is 1.70), 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 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
Per cent sulphate ash	21.4
Metal ratio	3.23

The following examples by comparison illustrate the substantial increase in metal content of the complex which is obtained by treating the mass with an acidic material before filtering to separate the desired product.

EXAMPLE 45

1700 grams of a 30% oil solution of barium petroleum sulphonate having a sulphate ash of 7.6% 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 added thereto, and the mixture was refluxed for one hour. The temperature was then raised to 160° C. over a period of 6 hours and maintained at that temperature for one hour. The mass was filtered and the product obtained was a liquid, brown in color, and contained a slight odor. The following properties of the products were determined:

Basic No.	66
Per cent sulphate ash	22.2
Metal ratio	3.64

EXAMPLE 46

1700 grams of a 30% oil solution of barium petroleum sulphonate having a sulphate ash of 7.6% were mixed with 134 grams of diisobutyl-phenol (ratio of equivalents is 1.7) and heated to 70° C. Then 800 cc. of H₂O and 302 grams of BaO were added and the mixture refluxed for one hour. The temperature was raised to 150° C. and maintained there for one hour. CO₂ was then injected therethrough at 150° C. and at a rate of

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1,650 cc./min. for 38 minutes. The mass was then cooled and filtered to separate the complex. The product was liquid, brown in color, and contained a faint odor. The following properties of the product were determined:

Basic No.....	5.05
Per cent sulphate ash.....	26.0
Metal ratio	4.52

EXAMPLE 47

400 lbs. of a 30% oil solution of barium petroleum sulphonate having a sulphate ash of 7.6% were heated to 80° C., and 32.5 lbs. of diisobutylphenol (ratio of equivalents is 1.67) were added thereto. Then 197 lbs. of water were added to the mixture, with stirring to insure thorough mixing. 73 lbs. of BaO were added thereto over a 30 minute period at 55–80° C. The mixture was agitated for about 10 minutes more at 80° C., then the temperature was raised to 100° C. and held there for one hour. Thereafter, the temperature was raised to about 150° C. and maintained at that level for one hour. Following this step, CO₂ was blown through the mass until about 75 lbs. thereof had been used over a period of three hours and at a temperature of 135–170° C. The mass was then filtered and the product was found to have the following properties:

Basic No.....	5.0
Per cent sulphate ash.....	25.7
Metal ratio	4.35

EXAMPLE 48

4590 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash, 363 grams of diisobutylphenol (ratio of equivalents is 1.7) and 2,800 grams of H₂O were heated to 60° C. 1,042 grams of BaO were added slowly and then the temperature of the mixture was raised to 94–98° C. and held there for one hour. Thereafter the temperature was raised to 150° C. in four hours, and maintained there for one hour. A small portion of the mass, 361 grams, was removed and filtered to give product A, whereas the remainder (5,296 grams) was blown with SO₂ at 170° C. until 330 grams thereof was used. This latter mass was then filtered and the product given below as product B was obtained. The analyses of products A and B are as follows:

	Product A	Product B
Basic No.....	63	4.5
Percent Sulphate Ash.....	19.5	29.5
Metal Ratio.....	3.18	5.35

From the foregoing examples it is shown that the method of treating the mass prior to filtering with an acidic material results in substantial increases in sulphate ash of the complex and thus correspondingly higher metal ratios.

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 of the present invention.

EXAMPLE 49

1700 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash were mixed with 61 grams of phenol (ratio of equivalents is 1.70) and the mixture was

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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 filtered 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 sulphate ash	21.2
Metal ratio	3.20

The sediment obtained in Example 49 was employed in the preparation of a salt complex in the method given in the following Example 50.

EXAMPLE 50

1700 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash, 20 grams of phenol, 450 grams of sediment obtained from the preparation given in Example 49, 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 sulphate ash	26.4

In the following examples, organic acids or salts thereof and inorganic alkaline earth metal compounds containing a metal other than barium were combined in the presence of a promoter to produce over based products.

EXAMPLE 51

1050 grams of a 45% oil solution of calcium petroleum sulphonate having a sulphate ash of 6.5% were mixed with 97.5 grams of para-tertiary-butyl phenol (ratio of equivalents is 1.54) and heated to about 80° C. To this mixture were then added about 148 grams of Ca(OH)₂ and about 300 cc. of water, and the total mixture was refluxed at about 100° C. for a period of two hours to insure thorough mixing. Thereafter the mass was heated to about 170° C. over a period of about four hours, then maintained at that temperature for 0.5 hour. The product was separated from the mass by filtration, and was found to be a liquid, brown in color and contained a faint odor. The following properties were determined for the product:

Basic No.	25.0
Percent sulphate ash	9.3
Metal ratio	1.57

EXAMPLE 52

1,050 grams of a 45% oil solution of calcium petroleum sulphonate having a sulphate ash content of 6.5% were mixed with 98 grams of para-tertiary-butyl phenol (ratio of equivalents is 1.54) and heated to about 70° C. To this mixture were added 112 grams of CaO and 300 cc. of water, and the total mixture was refluxed

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at the above temperature for about two hours to insure thorough mixing. Thereafter, the temperature was raised to about 160° C. over a period of about 5 hours and maintained there for about 0.5 hour. The product was separated by filtration and was found to be a liquid, brown in color, and having a faint odor. The following properties were determined for the product:

Basic No.	25.2
Percent sulphate ash	9.09
Metal ratio	1.53

EXAMPLE 53

1,120 grams of a 45% oil solution of calcium petroleum sulphonate having a sulphate ash content of 6.5%, 59 grams of 1-nitro-propane (ratio of equivalents is 1.52), 150 grams of $\text{Ca}(\text{OH})_2$ and 830 ml. of water were mixed together, and heated to about 100° C. for about one hour. The temperature was then raised to 150° C. and held at that level for one hour. The product was separated by filtering, and was found to be a viscous liquid, brown in color, and contained a faint odor. The product possessed the following properties:

Basic No.	36.1
Per cent sulphate ash	13.15
Metal ratio	2.36

For the purpose of comparison, calcium petroleum sulphonate was overbased with $\text{Ca}(\text{OH})_2$ in accordance with a conventional technique.

EXAMPLE 54

1,565 grams of a 30% oil solution of calcium petroleum sulphonate having a sulphate ash of 4.3% were mixed with a slurry of 37 grams of $\text{Ca}(\text{OH})_2$ and 150 cc. of water. The mixture was heated with stirring to 80-90° C. and held at that level for about one hour. The temperature was then raised to 160° C. and held at that level for about one hour. The product obtained was a viscous liquid, deep red in color, and had the following properties:

Basic No.	7.90
Per cent sulphate ash	5.15
Metal ratio	1.29

The following example illustrates the use of a different promoter when employing the calcium metal in the components:

EXAMPLE 55

A mixture of 459 grams of phenol, 244 grams of water and 90.5 grams of $\text{Ca}(\text{OH})_2$ was stirred at reflux temperature for two hours. Thereafter 1046 grams of a 45% oil solution of calcium petroleum sulphonate having a 6.7% sulfate ash (ratio of equivalents is 0.41) were added. The temperature of the mixture was then raised to 125° C., at which level substantially all of the water was removed. Prior to filtering the mixture, it was blown with CO_2 for three hours at a temperature of about 120-150° C. The complex was fluid, brown in color and did not contain any odor. The complex had the following analyses:

Basic No.	8.07
Per cent sulfate ash	18.35
Metal ratio	3.07

Another preparation was made in which dissimilar alkaline earth metals were present in the organic acid compound and inorganic metal compound. The following example illustrates this feature of the invention.

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EXAMPLE 56

1793 grams of a 45% oil solution of calcium petroleum sulphonate having a 6.45% sulfate ash, 206 grams of octyl phenol (ratio of equivalents is 1.7) and 954 grams of water were mixed together. Then 358 grams of BaO were added, and the mixture was agitated thoroughly. While insuring thorough mixing the temperature was raised to 90-100° C. for one hour. Thereafter, the temperature was raised to 150° C. over a two hour period and held at that level for one hour. The complex obtained by filtering the mixture had the following properties:

Basic No.	4.2
Per cent sulfate ash	25.2
Metal ratio	3.94

The complexes of this invention can be also obtained by using a mixture of oil soluble organic acid and the alkaline earth metal salt thereof. The following example illustrates this concept.

EXAMPLE 57

2875 grams of petroleum sulphonic acid and 6000 grams of a 30% oil solution of barium petroleum sulphonate (sulfate 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
Per cent sulfate ash	23.3
Metal ratio	3.73

EXAMPLE 58

1,000 grams of petroleum sulphonic acid, 98.1 grams of para-tertiary butyl phenol and 989 grams of water were mixed together and heated to 50° C. Thereafter, 258 grams of SrO were added to the mixture, the total mixture was raised in temperature to 100° C. and held at that level for about one hour. Thereafter, the total mixture was raised in temperature to about 150° C. and held at that level for about one hour. The product obtained was a viscous liquid, brown in color, and had the following properties:

Per cent sulphate ash	13.95
Metal ratio	1.67

The salt complexes formed with compounds containing barium metal possess exceptionally high metal ratios as compared to those complexes which are obtained when using other alkaline earth metal containing compounds. Consequently, in determining the maximum amount of metal which can be incorporated into a complex prepared by conventional techniques, the barium containing complexes were employed for such a purpose. Pursuant thereto, Examples 59 and 60 given below serve to show the highest amount of metal which can be incorporated into a salt complex by conventional techniques. Furthermore, the oil-soluble petroleum sulphonic acids are exceptionally better in producing high metal content salt complexes than other types of oil-soluble organic acid compounds.

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EXAMPLE 59

2500 grams of a 30% oil solution of barium petroleum sulphonate containing 7.6% sulphate 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
Per cent sulphate ash	16.0
Metal ratio	2.25

EXAMPLE 60

In this example the procedure employed in Example 59 was followed except that the dehydration step was conducted at a temperature of 200° C. for a period of one-half hour. The product obtained had the following properties:

Basic No.	29.0
Per cent sulphate ash	15.3
Metal ratio	2.16

From the above Examples 59 and 60 it can be seen that salt complexes obtained by conventional techniques will only have metal ratios as high as 2.25 or approximately 2.3. By comparison, the process of the present invention will in every instance, wherein a substantial amount of excess inorganic alkaline earth metal compound is employed, and when using the same organic acid compound, produce products containing more metal than is possible by any of the prior art techniques. Furthermore, in every instance where the salt complex produced by the process of this invention is treated with an acidic material and then distilled so as to remove substantially all of the ionizable organic compound, the remaining salt complex which constitutes essentially the promoter-free salt complex in combination with the acidic material, will have a higher ratio of total metal to metal in the normal salt of the organic acid than is possible with any prior art techniques. By Examples 63-74 inclusive given hereinafter, it will be shown that the treatment of the salt complex produced by the process of the present invention with an acidic material does not significantly affect the metal ratio of the complex. Furthermore, it is shown in those examples that the distillation of the thus acidic material treated complex so as to recover the ionizable organic compound does not significantly affect the metal ratio 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 61

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

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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
Per cent sulphate ash	25.5
Metal ratio	4.12

EXAMPLE 62

15530 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
Per Cent sulphate ash	15.34
Metal ratio	2.14

From the foregoing it will be noted that by following the process of the present invention, two types of metal complexes may be produced, both of which are different from any produced by any of the prior art processes. The first form of such complex is the immediate product with the promoter included therein in chemical combination. The second form of novel product is that which results from the treatment of the end product just described with an acidic material which has the effect, as stated above, of liberating the promoter from the complex without any substantial change in the metal ratio of the complex. The liberation of the promoter by this step of treating the first-named complex with an acidic material may be followed by a recovery, as by distillation, of the promoter thus liberated, leaving the end product and complex substantially free of the promoter material. A third product which is probably different from each of the two named above may be produced by treating the complex initially formed with an acidic material prior to the removal by filtration of the excess inorganic alkaline earth metal compound. When following this latter procedure, the promoter material is permitted to remain in the complex, and when this procedure is followed it has been found that unusually high metal ratios may be secured in the ultimate end product.

As previously indicated, the immediate end product formed by the use of the promoter material may be modified to recover therefrom a substantial portion of the promoter material used, by treating such immediate end 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 ionizable organic compound used as the promoter. After a portion of the promoter material has been thus regenerated by treating the immediate product with an acidic material, the regenerated promoter may then be separated therefrom by any one of the several known means, or the regenerated promoter 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.

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EXAMPLE 63

The salt complex produced in Example 43 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, CO₂ was blown through the mixture. The temperature was then lowered to 150° C., continuing the passage of CO₂ 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-CO₂ 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
Per cent sulphate ash.....	23.2

By comparison, the product of Example 43 contained a sulphate ash of 23.8% whereas this same product after blowing with CO₂ contained a sulphate ash of 23.2. Therefore, it can be seen that the metal ratio of the salt complex is substantially the same after treatment with CO₂.

EXAMPLE 64

6043 grams of the salt complex prepared in accordance with Example 9 were placed in a suitable vessel and CO₂ gas was injected at the bottom of the vessel at a rate of 3750 cc. per minute for a period of 1½ 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 311 grams. The product was fluid, dark red in color, and contained no odor. The following properties were determined for the salt complex-CO₂ product:

Basic No.....	4.3
Per cent sulphate ash.....	22.7

It can be seen, therefore, by the gain in weight of the product that the CO₂ actually enters into combination with the salt complex. Furthermore, the metal ratio of the product is substantially the same as the salt complex prior to being blown with CO₂, since the sulphate ash content is substantially the same as before CO₂ treatment.

EXAMPLE 65

1288 grams of the salt complex prepared in accordance with the method of Example 5 was blown with CO₂ at a temperature of 30-50° C. until the product showed an acid reaction. Following this CO₂ 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
Per cent sulphate 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. Furthermore, treatment with an acid-anhydride gas to such extent does not change the metal ratio of the salt complex, since the sulphate ash content is substantially the same as before treatment.

Another salt complex product which was blown with CO₂ is given in Example 66 below.

EXAMPLE 66

2500 grams of a 30% oil solution of barium

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petroleum sulphate containing 7.6% sulphate 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 sulphate ash.....	22.3
Metal ratio.....	3.34

EXAMPLE 67

1250 grams of the salt complex produced in accordance with the method given in Example 66 above were blown with CO₂ 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 CO₂-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 magnesium sulphate, filtered and then the magnesium sulphate was removed by filtration. 5 grams of residue remained. This residue was found to be phenol, thus indicating that treatment of the salt complex with an acidic material liberates at least a portion of the ionizable organic compound from complex formation.

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

Basic No.....	2.96
Percent sulphate ash.....	22.4

The percent sulphate ash of the CO₂-salt complex product indicates that little or no metal is removed from the complex as a result of the CO₂ treatment and the distillation step to recover the ionizable organic compound.

EXAMPLE 68

1440 grams of the salt complex obtained by the method given in Example 49 was blown with CO₂ for about two hours at a temperature of 30-60° C. until the product showed an acid number 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 contained a slight odor. This product possessed the following properties:

Basic No.....	1.06
Percent sulphate ash.....	22.6

Here again it is shown that the treatment of the salt complex with an acidic material liberates the promoter from complex formation. On a quantitative basis, it was determined that approximately ½ of the original phenol was still held in complex formation in the CO₂-treated product.

The salt complex prepared in accordance with Example 69 below was treated with SO₂ as shown in Example 70 which is given below.

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EXAMPLE 69

6000 grams of a 30% solution of barium petroleum sulphonate (sulphate 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 sulphate ash	26.0
Metal ratio	4.2

EXAMPLE 70

6623 grams of the product produced in accordance with Example 69 were treated with SO₂ 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 SO₂-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 CO₂ would be effective as an acidic material. The examples below illustrate the utility of air for this purpose.

EXAMPLE 71

380 lbs. of a 30% oil solution of barium petroleum sulphonate were mixed with 21.9 lbs. of para-tertiary-butyl phenol (ratio of equivalents is 1.7) and 184 lbs. of water. This mixture was heated to 50° C. and 68 lbs. of BaO were added over a period of 1½ hours while not permitting the temperature to go above 65° C. The total mixture was held at 100° C. for one hour, then heated to 150° C. over a period of 4.8 hours and held there for one hour. The desired product was fluid, dark red, and possessed the following properties:

Basic No.	80.5
Percent sulphate ash	26.0
Metal ratio	4.2

EXAMPLE 72

6000 grams of the product produced in Example 71 were placed in a 12-liter, 3-necked flask and heated to 175° C. The mass was then blown with air until a basic number of 1 was obtained. The final product contained a sulphate ash of 26.4% indicating substantially no change in the amount of metal present.

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 where-in the ratio of equivalents falls outside of said preferred range, but comes within the broad range found to be operable.

EXAMPLE 73

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

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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 one-half 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.
Per cent sulphate ash	27.9
Metal ratio	5.4

EXAMPLE 74

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.
Per cent sulphate ash	17.3
Metal ratio	2.4

It should be noted that in all of the specific examples given above, the mahogany soaps were referred to as either calcium or barium petroleum sulphonate, and likewise a similar designation was used for the mahogany acid.

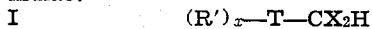
Component A—The oil soluble organic acid compounds used as starting materials

The organic compounds used as one of the starting materials in our process may be the oil soluble organic acids themselves and/or an alkaline earth metal salt thereof. At this point it should be noted that whereas Mertes found it necessary to first prepare a normal metal salt and then react such normal salt with an additional amount of a salt-forming material, our process can be carried on as a one-step process by beginning with the oil-soluble organic acid. While it is possible to first prepare the normal metal salt of the organic acid in the usual way, by a conventional salt-forming procedure, and then begin our process by utilizing such normal metal salt as one of the starting materials, it may be more convenient to employ as the starting material the organic acid rather than the salt thereof. Our process is operable for the production of certain types of compounds when utilizing as starting materials any of the products produced by the prior art processes. Also, as a starting material, mixtures of acids and salts can be used to produce the complex. The variety of classes of organic acids which can be employed are, for example, sulphur acids, carboxylic acids, phosphorus acids, etc. of the aliphatic and cyclic types, and the corresponding thio-acids.

More specific examples of organic acids are the sulphur acids including sulphonic, sulphamic, sulphinic, thiosulphonic, etc., and of these the sulphonic acids will find particular application under the present invention. A more specific identification of the sulphonic acids is given hereinbelow.

The carboxylic acids include the fatty acids

wherein there are present at least about 12 carbon atoms, such as, for example, palmitic, stearic, myristic, oleic, linoleic, etc. acids. The carboxylic acids of the aliphatic type can contain elements in the aliphatic radical other than carbon and hydrogen; examples of such acids are the carbamic acids ricinoleic acids, chlorostearic acids, nitro-lauric acids, etc. In addition to the aliphatic carboxylic acids, it is intended to employ the cyclic types such as those containing a benzenoid structure, i. e., benzene, naphthalene, etc., and an oil-solubilizing radical or radicals having a total of at least about 15 to 18 carbon atoms. Such acids are the oil-soluble aliphatic substituted aromatic acids as for example, stearyl-benzoic acids, mono- or polywax substituted benzoic or naphthoic acids wherein the wax group contains at least about 18 carbon atoms, cetyl hydroxy-benzoic acids, etc. The cyclic type of carboxylic acids also includes those acids which have present in the compound a cycloaliphatic group. Examples of such acids are petroleum naphthenic acids, cetyl cyclohexane carboxylic acids, di-lauryl deca-hydronaphthalene carboxylic acids, di-octyl cyclopentane carboxylic acids, etc. It is also contemplated to employ the thio-carboxylic acids, that is, those carboxylic acids in which one or both of the oxygen atoms of the carboxyl group are replaced by sulphur. These carboxylic and thio-carboxylic acids can be represented by the following formulae:



wherein R' is an aliphatic radical, x is at least 1, and (R')_x contains a total of at least about 15 to 18 carbon atoms; T is a cyclic nucleus such as benzene, naphthalene, diphenyl ether, diphenylene oxide, diphenyl sulphide, diphenylene sulphide, phenol, hydroxy-naphthalenes, phenol disulphides, petroleum naphthenes, cyclohexane, cyclopentane, chloro-cyclohexane, nitro-cyclopentane, deca-hydronaphthalene, mercaptodeca-hydro-naphthalene, etc.; and X is either oxygen or sulphur. In Formula II, R is an aliphatic group containing at least 12 carbon atoms and X is either oxygen or sulphur. R, R', and T can also contain other substituent groups such as nitro, amino, hydroxy, mercapto, halogen, etc. Representative examples are nitro-stearic acids, ceryl-chloro-salicylic acids, chloro-palmitic acids, cetyl-anthranilic acids, stearyl-mercaptanaphthoic acids, etc.

The phosphorus acids include tri- and pentavalent organic phosphorus acids and the corresponding thio-acids, which are, for example, phosphorous, phosphoric, thiophosphoric, thiophosphorous, phosphinic, phosphonic, thiophosphonic, thiophosphonic, etc. acids. Among the most useful of the phosphorus acids are those represented by the following formulae:



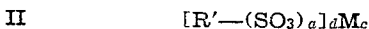
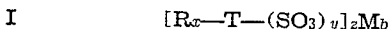
wherein X and X' are either oxygen or sulphur and at least one X and one X' is sulphur, and R and R' are each either the same or different organic radicals or hydrogen, and wherein at least one is an organic radical and at least one

R is hydrogen and wherein at least one R' is an organic radical and at least one R is hydrogen. Therefore, such formulae include the oil-soluble organic thio-acids of phosphorus, more particularly the organic thiophosphoric acids and the organic thiophosphorous acids. The organic radicals R and R' can be aliphatic, cycloaliphatic, aromatic, aliphatic- and cycloaliphatic-substituted aromatic, etc. The organic radicals R and R' preferably contain a total of at least about 12 carbon atoms in each of the above thio-acid types I and II. Examples of such acids are dicapryl dithiophosphoric acids, di-(methyl-cyclohexyl) dithiophosphoric acids, dilauryl dithiophosphoric acids, dicapryl dithiophosphorous acids, di-(methyl-cyclohexyl) dithiophosphorous acids, lauryl monothiophosphoric acids, di-(butylphenyl) dithiophosphoric acids, and mixtures of two or more of the foregoing acids.

Certain of the above described thio-acids of phosphorus such as for example di-capryl dithiophosphoric acid are also commonly referred to as acid esters.

As indicated, our process is applicable not only when using the oil-soluble organic acid as such as one of the starting materials, but also the alkaline earth metal salts of such organic acids. The present process will produce a high metal content organo metallic material when as one of the starting materials one uses any of the metal organic complexes produced by the prior art workers, such as for example, Bergstrom, Griesinger, Campbell et al., and Mertes. We thus may utilize as a starting material the end product produced by these prior art workers and from them produce the novel high metal content complex of our invention.

From the broad class of available organic acid compounds, it is preferred to employ the oil-soluble sulphonic acid compounds. Furthermore, of the available alkaline earth metal salts of organic acids, the barium salts thereof are preferred for the reason that unexpectedly excellent results are obtained by the use thereof. These oil-soluble sulphonic acids, and the alkaline earth metal salts thereof can be represented by the following structural formulae:



In the above formulae M is either an alkaline earth metal, preferably barium, or hydrogen; T is a cyclic nucleus either of the mono- or polynuclear type including benzenoid or heterocyclic nuclei such as benzene, naphthalene, anthracene, phenanthrene, diphenylene, thianthrene, phenothioxine, diphenylene sulphide, diphenylene oxide, diphenyl oxide, diphenyl sulphide, diphenyl amine, etc.; R is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxy-alkyl, carboalkoxy-alkyl, or aralkyl groups, x is at least 1, and R_x contains a total of at least about 15 to 18 carbon atoms; R' in Formula II is an aliphatic radical containing a total of at least about 15 to 18 carbon atoms, and M is either an alkaline earth metal, preferably barium, or hydrogen. When R' is an aliphatic substituted cycloaliphatic group, the aliphatic substituent should contain a total of at least about 12 carbon atoms. Examples of types of the R' radical are alkyl, alkenyl, and alkoxy-alkyl radicals, and aliphatic substituted cycloaliphatic radicals where the aliphatic group is alkyl, alkoxy, alkoxy-alkyl, carboalkoxyalkyl, etc. Specific examples of R' are cetyl-cyclohexyl, lauryl-cyclohexyl, ceryloxyethyl, and oc-

tadecenyl radicals, and radicals derived from petrolatum, saturated and unsaturated paraffin wax, poly olefins, including poly-C₃, C₄, C₅, C₆, C₇, C₈, olefin hydrocarbons. The groups T, R and R' in the above formulae can also contain other organic or inorganic substituents in addition to those enumerated above, such as for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, carboxy, ester, etc.

In Formula I above, x , y , z and b are at least one; whereas in Formula II a , d , and c 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 alkaline earth metal salts of the sulphonic acids. In other words, for every sulphonic acid, it is intended that the alkaline earth metal salt thereof is also illustrated. This includes specifically, the barium, strontium, calcium and magnesium salts of the hereinbelow illustrated sulphonic acids.

Such sulphonic acids are mahogany sulphonic acids; petrolatum sulphonic acids; mono- and polywax substituted naphthalene sulphonic, phenol sulphonic, diphenyl ether sulphonic, diphenyl ether disulphonic, naphthalene, disulphide sulphonic, naphthalene disulphide disulphonic, diphenyl amine disulphonic, diphenyl amine sulphonic, thiophene sulphonic, alpha-chloro-naphthalene sulphonic acids, etc.; other substituted sulphonic acids such as cetyl chloro-benzene sulphonic acids, cetyl-phenol sulphonic acids, cetyl-phenol disulphide sulphonic acids, cetyl-phenol mono-sulphide sulphonic acids, cetoxy capryl-benzene sulphonic acids, di-cetyl thianthrene sulphonic acids, di-lauryl beta-naphthol sulphonic acids, and 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, tetra-amylene 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-cyclo-hexyl sulphonic acids, bis-(diisobutyl)-cyclohexyl sulphonic acids, mono- and poly-wax substituted cyclo-hexyl sulphonic acids, etc.

With respect to the sulphonic acids, it is intended herein to employ the term "petroleum sulphonic acids" to cover all sulphonic acids which are derived from petroleum products. Additional examples of sulphonic acids and/or alkaline earth metal salts thereof which can be employed 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.

Of the various types of organic acids and alkaline earth metal salts thereof enumerated above, i. e. sulphur acids, carboxylic acids, phosphorus acids, etc., it is preferred to employ the sulphur-bearing organic acids or alkaline earth metal salts thereof. However, it is to be understood that all of organic acids and salts thereof are not equivalent in their ability to complex with unusual amounts of inorganic alkaline earth metal compounds in the presence of a promoter, because under certain conditions, some organic

acids or salts thereof are more effective than others.

Component B—The promoter material

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 alkaline earth metal 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 either oxygen or sulfur. Also the alkaline earth metal 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 0.0005% at 50° C. and saturated aqueous solutions of which at about 25° C. exhibit a pH not greater than seven.

Generally, the ionizable organic compound or the alkaline metal salt thereof include a variety of classes of compounds such as, for example, phenolic compounds, enolizable organic nitro compounds, e. g., nitro-paraffins, 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. To better illustrate the wide variety of classes of compounds which can be employed in forming the salt complexes in accordance with the present invention, specific examples are enumerated below. It is to be understood that while only the ionizable organic compounds are illustrated, it is intended that the alkaline earth metal salts thereof are included as specific examples. More specifically, the calcium, barium, strontium, and magnesium salts of such illustrated ionizable organic compounds are intended.

The "phenolic compound" referred to hereinabove is for the purpose of this specification and the appended claims an organic compound having a hydroxyl group attached directly to a carbon atom of a benzenoid ring, and which compound is with or without other substituents on the benzenoid ring. It should likewise be understood that "a phenol" is a sub-class of a phenolic compound, in which there is only a hydroxyl group on the benzene ring or in addition to the hydroxyl group, there is also present in the molecule a single hydrocarbon group or a plurality thereof. Those phenolic compounds containing not more than 30 carbon atoms in the molecule are preferred as promoters.

The ionizable organic compounds found useful as promoters are phenol; alkylated phenols such as, for example, cresols, xylenols, p-ethyl phenol, di-ethyl phenols, n-propyl-phenols, di-isopropyl-phenols, p-t-butyl-phenol, p-t-amyl-phenol, p-cyclopentyl-phenol, p-(4-methyl-cyclohexyl)-phenol, sec-hexyl-phenols, n-heptyl-phenols, diisobutyl-phenols, 3,5,5-tri-methyl-n-hexyl-phenols, n-decyl-phenols, cetyl-phenols, etc.; aryl substituted phenols, e. g., phenyl phenol, diphenyl phenol, etc.; poly-hydroxy aromatic compounds such as alizarin, quinizarin or polyhydroxy-benzenes, e. g., hydroquinone, catechol, pyrogallol, etc.; mono-hydroxy naphthalenes, e. g., α -naphthol, β -naphthol, etc.; poly-hydroxy naphthalenes, e. g., naphthohydroquinone, naphthoresorcinol, etc.; the alkylated polyhydroxy-aromatic compounds such as octyl-catechols, triisobutyl-pyrogallols, etc.; substituted phenols such as p-nitro-phenol, picric acid, o-chloro-

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 acids, etc., whereas 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, SO₂, SO₃, CO₂, air (considered acidic because of CO₂ content), NO₂, H₂S, N₂O₃, PCl₃, SOCl₂, ClO₂, H₂Se, BF₃, CS₂, COS, etc.

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

The complex of the present invention can be produced by using the same alkaline earth metal in the organic acid compound, promoter and inorganic compound; or such complexes can be derived from components containing dissimilar alkaline earth metals. In some instances it is desirable to employ a mixture of organic acid compounds which contain at least two or up to and including four dissimilar alkaline earth metals; or the same distribution of metals can be obtained by varying the type of promoter and/or inorganic compound in various combinations with the organic acid compound. It is therefore possible to employ various combinations of dissimilar alkaline earth metals in the starting materials used in preparing the complex product.

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 metal compound. However, more usually about 5 to 50, and preferably about 15 to 30, moles of water per mole of inorganic metal compound are used.

Generally the complex formed with the inorganic alkaline earth metal compound, the oil-soluble organic acid or the alkaline earth metal 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 the organic acid, followed by addition of an aqueous solution or suspension of the inorganic alkaline earth metal 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 water which might be present;

(b) The inorganic alkaline earth metal compound in a dry state is added to a mixture of organic acid or a normal salt of such organic acid, 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 salt of organic acid is mixed with the promoter, then an aqueous solution or suspension of the inorganic alkaline earth metal 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 any of the methods discussed herein for preparing the salt complex, a substantial increase in metal content is usually effected by treating the mass containing the complex product with an acidic material just after substantial amounts of water are driven off and just before the mass is filtered.

(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 which is present is accomplished at a temperature not substantially in excess of 350° C., preferably about 110° C. 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 sub-atmospheric pressure as well as heating under either atmospheric or superatmospheric pressure. At a later stage, the acidic material when used in gaseous form, may be used to remove the last portion of water. 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 amount of material being processed and on the technique employed therefor. Generally, the time required to effect substantial removal of water is at least about 15 minutes or less and can be as high as 10-15 hours or more. 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 from the process mixture. It was observed that satisfactory complexes are obtained when using any of the techniques described above, and that the final water content can be up to about 2% or more.

Usually, as indicated above, the components are combined and agitated at an elevated temperature to insure thorough mixing, and then water is removed therefrom. It should be understood that the process to form the complex can be effected without the preliminary heating and mixing period, if desired. It is therefore not essential to this invention to have such a preliminary step because all that appears necessary is to mix the components and remove substantially any water which is present.

For the purposes of this specification and the appended claims, the relative amounts of oil-soluble organic acid or the alkaline earth metal salt thereof and promoter is expressed in the "ratio of equivalents" of the former to the latter. In accordance therewith, the ratio of equivalents of oil-soluble organic acid or the alkaline earth metal salt thereof to promoter is from about 1 to 10 to about 10 to 1, more usually from about

phenol, 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-silicylic acids, gallic acid, 4-hydroxy-1-naphthoic acid, etc.; lower molecular weight aromatic sulphononic acids such as p-cresol sulphononic acids, p-t-butyl-phenol sulphononic acids, beta-naphthol alpha-sulphononic acid, etc.; lower molecular weight aromatic carboxylic acids such as benzoic acid, p-nitro-benzoic acid, o-chlorobenzoic acid, p-toluic acid, p-t-butyl-benzoic acid, alpha-naphthoic acid, etc.; lower molecular weight aromatic sulphononic acids such as benzene sulphononic acid, p-chlorobenzene sulphononic acid, p-nitrobenzene sulphononic acid, p-tolyl sulphononic acid, p-t-butyl-benzene sulphononic acid, t-amyl-naphthalene sulphononic acids, etc.; lower molecular weight aliphatic sulphononic acids such as ethyl sulphononic acid, beta-chloro-ethyl sulphononic acid, gamma-nitro-propyl sulphononic acid, octyl sulphononic acids, chlorodi-isobutyl sulphononic acids, diisobutenyl sulphononic acids, etc.; nitroparaffins such as 1-nitro propane, 2-nitro-n-butane, 1-nitro-1-(p-diisobutyl-phenoxy) propane, etc.; lower molecular weight thio-acids of phosphorus including aliphatic dithiophosphoric acids, e. g., di-isopropyl dithiophosphoric acid, di-n-butyl dithiophosphoric acids, etc., aromatic dithiophosphoric acids, e. g., di-(phenyl) dithiophosphoric acids, etc., the aliphatic mono thiophosphoric acids, e. g., di-ethyl monothiophosphoric acids, etc., the aromatic monothiophosphoric acids, e. g., di-tolyl monothiophosphoric acids, di-(iso-propyl-phenyl) monothiophosphoric acids, etc.

Additional examples of compounds which can be employed as promoters are given 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 ionizable organic compounds and the alkaline earth metal salts thereof are not all equivalent as promoters, but that under certain conditions some are more effective than others.

Component C—The alkaline earth metal salt-forming compounds

The salt-forming compounds which are employed to impart to the process mass the specified amount of metal may be broadly defined as inorganic alkaline earth metal compounds wherein anionic radicals may be, for example, hydroxyl, oxide, carbonate, bi-carbonate, sulphide, hydrosulphide, halide, hydride, amide, basic carbonate, etc. Of the inorganic alkaline earth metal 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%. Still more preferred are those inorganic alkaline earth metal compounds, saturated aqueous solutions of which give an alkaline reaction or pH value greater than 7.

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

The alkaline earth metal inorganic compounds include the barium containing compounds such as barium hydroxide, barium oxide, barium sulfide, barium carbonate, barium bi-carbonate,

barium hydride, barium amide, barium chloride, barium bromide, barium nitrate, barium sulfate, barium borate, etc.; the calcium containing compounds such as calcium hydroxide, calcium oxide, calcium sulfide, calcium carbonate, calcium bicarbonate, calcium hydride, calcium amide, calcium chloride, calcium bromide, calcium nitrate, calcium borate, etc.; the strontium-containing compounds such as strontium hydroxide, strontium oxide, strontium sulfide, strontium carbonate, strontium bicarbonate, strontium amide, strontium nitrate, strontium hydride, strontium nitrite, etc.; the magnesium-containing compounds such as magnesium hydroxide, magnesium oxide, magnesium carbonate, magnesium bicarbonate, magnesium nitrate, magnesium nitrite, magnesium amide, magnesium chloride, magnesium sulfate, magnesium hydrosulfide, etc. The corresponding basic salts of the above described compounds are also intended, however, it should be understood that the inorganic alkaline earth metal compounds are not equivalent for the purposes of the present invention, because under certain conditions some are more effective or desirable than others.

The acidic material

As previously indicated, one form of the process of the present invention includes the step of treating the immediate complex product with an acidic material for the purpose of liberating therefrom at least a portion of the material previously referred to as the promoter. 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 above-identified 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 carbon dioxide or air has the effect of freeing 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 complex product from any metal organic complex type material heretofore produced. Moreover, the nature of the product formed by regenerating from the immediate end product at least a portion of the promoter material leaves that complex with a composition which is quite different from the other prior art metal organic complexes previously produced. It is recognized that in accordance with the present invention, the alkaline earth metal salt of the ionizable organic compound can be employed as the promoter in forming the salt complex. However, when such a salt is used as the promoter and the resulting complex is treated with an acidic material, the metal-free ionizable organic compound is freed from its salt.

For the purpose of releasing the ionizable organic compound used as a 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 higher than the ionizable 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,

1 to 1 to about 10 to 1, and preferably from about 3 to 2 to about 7 to 2.

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

As indicated hereinabove, treatment of the salt complex 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 ionizable organic compound. This treatment is effected at a temperature of from about 25 to 250° C., preferably from about 50 to 170° C. and usually employing from 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 may cause only partial liberation or release of ionizable organic compound 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 or more. 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.

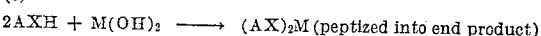
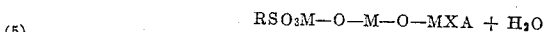
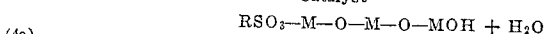
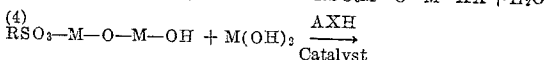
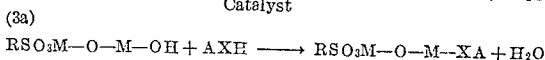
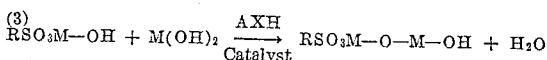
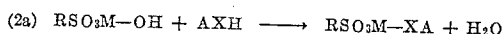
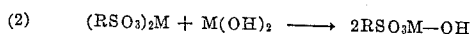
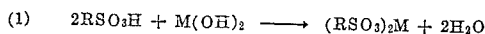
To substantially increase the metal content of the salt complex, it may be desirable to treat the total mass with an acidic material just prior to filtering same. This treatment may conveniently be effected at a temperature of from about 25° to 250° C. preferably from about 50° to 170° C., using from about 0.5 to 20% of acidic material, based on the total mass, and for a period of from about 0.25 to 30 hours. The acidic material employed is preferably an acid anhydride gas, as defined hereinabove. Treatment with the acid anhydride gas may be accelerated by superatmospheric pressure.

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 organic acid. In accordance therewith, the salt complex as of this invention will have metal ratios greater than 1 and up to 10 or more, preferably from about 2 to 8. As for the finished

salt 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 ratios as given above will apply to such treated product. In those instances where the finished 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.

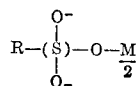
By reason of the high metal ratio of the complexes produced in accordance with this invention, the following theories are suggested as a possible explanation of how the metal is combined. It is to be understood, however, that such theories are advanced for the purpose of offering explanations, and are 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. $(-M-O-)_nH$, 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:



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.

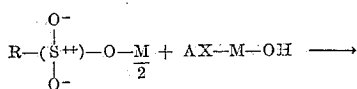
Another theory is based upon an electronic interpretation. For example, in the case of the neutral sulphonate, the charges are distributed as follows:



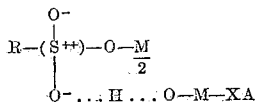
The electron octets around the two oxygen atoms which are not attached to a metal atom give to each of these atoms a unit negative charge, thus leaving the sulphur atom with a double positive charge.

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:

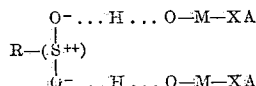


(a)



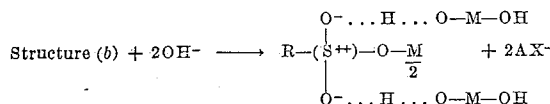
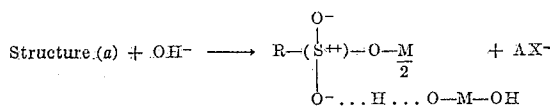
and

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



The AX^- ions may then react with $\text{M}(\text{OH})_2$ to produce more $\text{AX}-\text{M}-\text{OH}$, 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 $\text{AX}-\text{M}-\text{OH}$ appears to function as a carrier for the $\text{M}(\text{OH})_2$, and thus facilitating the communicating of the $\text{M}(\text{OH})_2$ 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, fireproofing and stabilizing agents in plasticizers and plastics, paint driers, rust inhibiting compositions, pesticides, foaming compositions, cutting oils, metal-drawing compositions, flushing oils, textile treatment compositions, tanning assistants, metal cleaning compositions, emulsifying agents, antiseptic cleansing compositions, penetrating agents, gum solvent compositions, fat splitting agents, bonding agent for ceramics and asbestos, asphalt improving agents, flotation agents, improving agents for hydrocarbon fuels such as e. g., gasolene and fuel oil, etc.

More particularly, the complexes of this inven-

tion are especially adapted for the preparation of lubricants, paint driers and plastics, particularly 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
Lubricant.....	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:

Per cent by weight

Use in a lubricant:	
SAE 20 motor oil	95.0
Product of Example 47	4.0
P ₂ S ₅ -treated turpentine	0.5
Zinc di-n-hexyl dithiophosphate	0.5

Use as a stabilizing agent for halogen-bearing plastics:

Poly-chloroprene	40.0
Di-lauryl sebacate	59.25
Product of Example 58	0.75

Use as a paint drier:

Enamel (alkyd resin)	98.5
Product of Example 55	1.5

This application is related to our copending applications Ser. No. 216,101, filed March 16, 1951; Ser. No. 216,102, filed March 16, 1951; Ser. No. 224,458, filed May 3, 1951; Ser. No. 263,961, filed December 28, 1951; Ser. No. 263,962, filed December 28, 1951; Ser. No. 263,963, filed December 28, 1951; Ser. No. 276,462, filed March 13, 1952; and Ser. No. 279,285, filed March 28, 1952.

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:

- An oil-soluble organic acid compound containing at least 12 carbon atoms in the molecule selected from the class consisting of the aliphatic and cyclic; sulphur acids, carboxylic acids, phosphorus acids, the thio acids corresponding to any of the foregoing acids, and the alkaline earth metal salts of any of said acids;
- An organic compound selected from the class consisting of phenolic organic compounds and the alkaline earth metal salts thereof, said phenolic organic compounds having
 - An ionization constant in water of at least about 1×10^{-10} at about 25° C.;
 - A water solubility at 50° C. of at least about 0.0005%; and
 - 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 alkaline earth metal 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 alkaline earth metal, including the alkaline earth metal 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 alkaline earth metal complex; and then treating the organic alkaline earth metal complex with an acidic material of which the ionization constant is higher than the ionization constant of the organic salt-forming compound of component B and in amounts sufficient to liberate a substantial proportion of said organic compound of component B.

2. The process set forth in claim 1 wherein the active component B is diisobutyl phenol.

3. The process set forth in claim 1 wherein the active component B is an alkaline earth metal salt of diisobutyl phenol.

4. The process set forth in claim 1 wherein the active component B is tertiary-butyl-phenol.

5. The process set forth in claim 1 wherein the active component B is phenol.

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

7. A process in accordance with claim 1 characterized further in that the organic compound which is component B is a hydrocarbon substituted phenol in which the hydrocarbon radical has not more than about 16 carbon atoms.

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

9. A process in accordance with claim 1 characterized further in that the organic compound which is component B is an alkaline earth metal salt of a phenolic organic compound.

10. A process in accordance with claim 1 characterized further in that the organic compound which is component B is an alkaline earth metal salt of a hydrocarbon substituted phenolic organic compound in which the hydrocarbon radical has not more than about 16 carbon atoms.

11. A process in accordance with claim 1 characterized further in that the organic compound which is component B is an alkaline earth metal salt of a lower alkyl substituted phenolic organic compound.

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

13. 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.

14. 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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THOMAS W. MASTIN.
ALAN RHODES.

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