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# PREPARATION OF COMPLEX CARBONATED METAL SALTS OF ALKYL PHENOL SULFIDES AND MINERAL OIL FRACTIONS CONTAINING THE SAME

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This invention is directed to complex carbonated metal salts of alkyl phenol sulfides and to a process for preparing such salts. The invention also contemplates the use of these salts as addition agents for various mineral oil fractions, particularly mineral lubricating oils.

It is well known that lubricating oils tend to deteriorate under the conditions of use in present day diesel and automotive engines with attendant formation of sludge, lacquer and resinous materials which adhere to the engine parts, particularly the piston ring grooves and skirts, thereby lowering the operating efficiency of the engine. To counteract the formation of these deposits, certain chemical additives have been found which when added to lubricating oils have the ability to keep the deposit-forming materials suspended in the oil, so that the engine is kept clean and in efficient operating condition for extended periods of time. These addition agents are known in the art as detergents or dispersants. Metal organic compounds are particularly useful in this respect. These metal organic compounds are considered to be effective on the basis of their metal contents, coupled with their solubility in the oil. Generally, it has been found that the oil-soluble metal organic compounds having the greater percentages of metal provide the better detergents. On this basis, it has been sought to provide detergent compounds having the highest possible metal contents. Metal phenates, particularly metal phenate sulfides, have been found to be effective detergents for mineral lubricating oils. The art, therefore, has sought to still further enhance the effectiveness of these compounds by increasing their metal contents. The present invention is concerned with the provision of a new class of metal alkyl phenol sulfides, referred to herein as complex carbonated metal alkyl phenate sulfides, which have exceptionally high metal contents and which are highly superior oil detergents. The metal contents of these new complex salts range from at least about 50 to at least about 250% higher than the metal contents of the corresponding normal metal phenate sulfide salts, i.e., salts having metal contents equivalent to the phenol hydroxyl contents of the corresponding phenol sulfides from which they are derived. Besides being excellent detergents, these new complex salts are also effective antioxidants for lubricating oils. Furthermore, their utility is not limited to use in lubricating oils as they are also effective additives for fuel oils and gasoline. Thus, in fuel oils, they inhibit sludge formation brought about by oxidation of the fuel in storage and they are effective anti-screen clogging agents. They are also useful as anti-rust agents in gasoline.

It is, therefore, the primary object of this invention to provide a new class of compounds, viz., complex carbonated metal salts of alkyl phenol sulfides. It is a further object to provide petroleum oil fractions of improved characteristics, said fractions containing minor amounts of these complex salts. It is a specific object to provide lubricating oil compositions containing these



complex salts which compositions are characterized by high detergent ability. It is a further object to provide fuel oil compositions containing these products, said fuel oil compositions having improved anti-sludging and anti-clogging characteristics. It is also an object to provide gasoline compositions containing these complex salts, said compositions being resistant to the formation of rust therein.

Broadly, the method by which the complex carbonated metal phenate sulfide salts are produced in accordance with the invention comprises reacting an alkyl phenol sulfide with a metal alcoholate in a proportion to provide from at least 1.2 to about 1.6 equivalents of metal per equivalent of phenol hydroxyl in the phenol sulfide reactant, reacting the resulting product with carbon dioxide and then reacting the carbonated product with additional metal alcoholate in an amount to supply from about 0.6 to about 1.0 equivalent of metal per equivalent of phenol hydroxyl in the phenol sulfide reactant. More specifically, the method of the invention may be carried out as follows. The alkyl phenol sulfide and a diluent solvent, such as a mineral oil, are charged to a suitable reactor, such as a round-bottomed flask, fitted with a mechanical stirrer, a dropping funnel and a condenser arranged for take-off of condensate. The use of a diluent solvent has been found advantageous due to the fact that the alkyl phenol sulfide reactant as well as the complex salt products are generally quite viscous. The oil reduces the viscosity of the reaction mixture and greatly facilitates the process, particularly the carbonation step and the final filtration and handling of the product. Any of the known hydrocarbon solvents of suitable boiling range, such as mineral oil, petroleum naphtha, or the like may be used. The use of a mineral oil, however, is preferred, since it need not be removed from the final product, the oil solution of the product thus obtained being directly blendable with a lubricating oil or other petroleum fraction desired to be improved therewith.

The metal alcoholate reagent is slowly added to the phenol sulfide-oil blend with continuous stirring while the reaction mixture is heated at a temperature sufficient to distill off alcohol. Depending upon the alcoholate used, the temperature of the reaction may range from about 80° C. to 150° C. After the metal alcoholate has been added, the temperature of the reaction mixture is increased to from about 125° C. to about 200° C. and the mixture is swept with nitrogen for about ½ hour to complete the reaction and removal of uncombined alcohol. The nitrogen is then replaced by carbon dioxide which is passed into the reaction mixture for several hours at the 125° C. to 200° C. temperature level. The reaction mixture is then cooled to 80° C. to 150° C. and additional metal alcoholate is added slowly through the dropping funnel with continuous removal of alcohol. The temperature is then again raised to the 125° C. to 200° C. level and the reaction mixture swept with nitrogen at this temperature to remove uncombined alcohol. The product is recovered by adding about 5 weight percent of "Hyflo" (a diatomaceous earth filter aid) to the reaction mixture, which is then filtered through an electrically heated Büchner funnel which has been precoated with "Hyflo." Before final filtration the product may be subjected to further carbonation and further reaction with metal alcoholate whereby still further amounts of metal are incorporated therein. Also, final carbonation treatment may be applied to the product without lessening the metal content thereof.

As previously indicated, the products provided in the process are concentrated oil solutions which usually contain from about 30% to about 70%, by weight, of the complex carbonated alkyl phenate sulfide salts and they may be utilized as such for addition to mineral oil frac-

tions in amounts to improve the various properties thereof. Where a volatile solvent rather than a mineral oil is used as the solvent in the process it may be readily removed by distillation.

As already indicated, the amount of metal alcoholate employed in the pre-carbonation step of the process should be that which will provide from at least 1.2 to about 1.6 equivalents of metal per equivalent of phenol hydroxyl in the phenol sulfide reactant. Thus, it has been found that when the alcoholate is employed in amounts to provide less than 1.2 equivalents of metal, the high metal content complex salt products are not obtained in the process. On the other hand, the use of amounts of metal alcoholate which provide more than 1.6 metal equivalents does not significantly increase the metal contents of the complex salt products. The highest metal contents in the final products, however, are obtained by the use of the metal alcoholate reagent in an amount to provide about 1.6 metal equivalents to the reaction. The use of such latter amounts in this step of the process is, therefore, preferred.

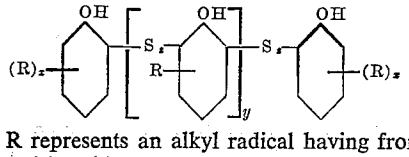
The carbonation step should be carried out for a time sufficient to allow from at least about 0.2 to at least about 0.6 equivalent of carbon dioxide per equivalent of phenol hydroxyl to be incorporated into the final product. Where the carbonation step is conducted by blowing the carbon dioxide through the reaction mixture the carbonation treatment may take several hours. However, it will be appreciated that with more efficient contacting of the carbon dioxide with the reaction mixture, such as by the use of a pressure reactor, the carbonation time may be substantially reduced.

The metal alcoholate charged after the carbonation step should be that sufficient to supply from at least about 0.6 to about 1.0 equivalent of metal, the preferred amount being about 0.6 equivalent. In this connection, it has been found that the highest amount of metal is incorporated into the complex salt product when about 1.6 equivalents of metal is charged in the precarbonation step and about 0.6 equivalent is charged in the post-carbonation step of the process. Accordingly, this procedure is preferred in the invention. See Example 4 herebelow.

In general, the ratio of phenol hydroxyl to carbon dioxide to metal in the products of the invention ranges from about 0.2 to about 0.6 equivalent of carbon dioxide to from about 1.6 to about 2 equivalents of metal for each equivalent of phenol hydroxyl in the phenol sulfide reactant. With repeated carbonation and metal alcoholate reaction steps, however, these ratios can be raised to as high as about 1.70 equivalents of carbon dioxide and about 3.6 equivalents of metal per equivalent of phenol hydroxyl in the phenol sulfide reactant.

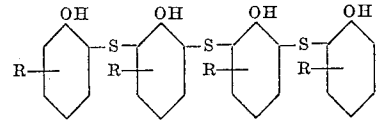
## THE PHENOL SULFIDE REACTANT

The phenol sulfides to which the method of the invention can be applied to form the complex carbonated phenate sulfide salts are alkyl phenol sulfides of the class represented by the general formula:



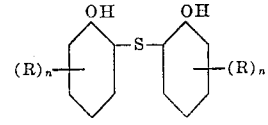
wherein R represents an alkyl radical having from about 5 to about 24 carbon atoms, $x$ represents an integer from 1 to 4, $y$ represents an integer from 0 to 3 and $z$ represents an integer from 1 to 5. As is well known, the various alkyl phenol sulfides coming within the aforesaid formula may be prepared by reaction of the various alkylated phenols with either sulfur monochloride or sulfur dichloride in various proportions. In these reactions the proportions of alkyl phenol and sulfur chloride used affects the type of product produced. The following are illustrative of the types of products which may be obtained using sulfur dichloride: (1) A product prepared by the reaction of 4 mols of a monoalkyl-substituted phenol with 3 mols of sulfur dichloride:





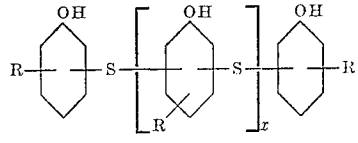
where R represents an alkyl radical.

(2) A product prepared from 2 mols of an alkyl phenol with 1 mol of sulfur dichloride:



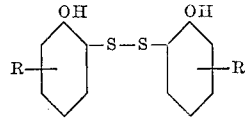
where R represents an alkyl radical and $n$ is an integer from 1 to 4.

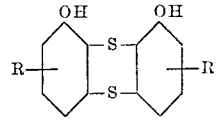
(3) A product prepared from an alkyl phenol with sulfur dichloride in a 1:1 mol ratio:



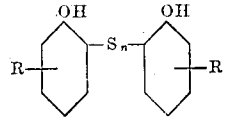
where R represents an alkyl radical and $x$ is an integer of 2 to about 6. These products are usually referred to as phenol sulfide polymers.

It will be understood that although the types of compounds above-illustrated represent the principal phenol sulfide products provided by the reacting proportions of alkyl phenol and sulfur dichloride specified, the products in all cases are actually mixtures of various phenol sulfides containing at least small amounts of di- and polysulfides, such as the following:





and



where R is alkyl and $n$ is an integer from 3 to 6.

As ordinarily manufactured on a commercial basis the phenol sulfides are prepared from mixtures of alkyl phenols and not from pure compounds. It will be understood then that the present invention has application to phenol sulfides in general, including specific relatively pure alkyl phenols as well as mixtures thereof.

Of the various phenol sulfides, the mono-substituted alkyl phenol sulfides in which the alkyl group contains from about 5 to about 24 carbon atoms and is in the para position on the ring are preferred. Nonylphenol sulfide, prepared by reaction of 4 mol proportions of nonylphenol and 3 mol proportions of sulfur dichloride is particularly preferred. Other specific alkyl phenol sulfides highly useful in the invention are the following: monooctyl phenol sulfide, monodecyl phenol sulfide, diamyl phenol sulfide, dodecyl phenol sulfide, dinonyl phenol sulfide, hexadecyl phenol sulfide, octadecyl phenol sulfide and wax phenol sulfide.

## THE METAL ALCOHOLATE REAGENT

The metal alcoholate reagents which have been found useful in the method of this invention are those prepared by the reaction of a metal oxide, or metal per se, with a lower aliphatic alcohol, such as methyl, ethyl, propyl or butyl alcohol, according to one of the following equations:

(1) $BaO+ROH \rightarrow Ba.OH(OR)$

(2) $2Na+2ROH \rightarrow 2NaOR+H_2$

(3) $Mg+2ROH \rightarrow Mg(OR)_2+H_2$

where R in all instances represents a lower alkyl radical of from 1 to about 4 carbon atoms, such as methyl, ethyl, propyl and butyl radicals. Up to the present time only the alcoholates of sodium, barium and magnesium have been found to provide the high metal content phenate sulfide salt products. It is believed, however, that alcoholates of other metals may function in the process. Of the several alcoholates which have been utilized successfully, barium methylate, Ba.OH(OR), is preferred, both from the economic standpoint as well as its ease of processing and the superior performance of the barium complex salt products as oil detergents.

## NATURE OF THE COMPLEX CARBONATED METAL ALKYL PHENATE SULFIDE PRODUCTS

The exact manner in which the metal alcoholate and carbon dioxide combine with the phenol sulfides to form the complex carbonated metal alkyl phenol sulfide salts of the invention is not known and the salt products are, therefore, defined herein by their method of preparation. It has been found, however, that all of the salts release carbon dioxide when treated with mineral acid. This indicates a structure in which the carbon dioxide exists as carbonate or bicarbonate. Also, typical base number curves of the products show three plateaus, indicating the presence of (1) a relatively highly basic component which is probably metal alcoholate and/or hydroxide, (2) a component of intermediate alkalinity, which is presumably metal phenate and (3) a component of relatively weak basicity, which is probably metal carbonate or bicarbonate. In the case of the barium complex salts, analysis has shown no carbon dioxide to be present as carboxyl substituent on the benzene ring. In the case of the sodium salts, however, it has been found that when the carbonation step of the process is conducted at a temperature of about 200° C., or higher, the complex salt does contain carboxyl groups on about 20% of the phenol rings in addition to that which is present in the form of carbonate or bicarbonate. Carbonation at lower temperatures, however, i.e., about 125° C., produces only a slight amount of carboxylation, as indicated by infrared analysis.

All of the products have been found to contain a significant amount of alcoholate substituent. Without intending to limit the invention by theoretical considerations, therefore, it can be said that the complex salts provided by the process of the invention are multi-component complexes comprised essentially of metal phenate, metal carbonate or bicarbonate and metal alcoholate and/or metal hydroxide. Rather than being combined in any fixed ratio, however, the ratio of components varies as the reactant ratios are changed. Assignment of a definite structure to the products is, therefore, not feasible.

It is recognized that high metal content carbonated alkyl phenate sulfide salts of a somewhat similar nature to the complex salts of this invention have been shown in the prior art. Thus, British Patent No. 744,942 discloses the formation of high barium content phenate and phenate sulfide salts. The method of that patent, however, involves, as an essential step, the "neutralization" of the alkyl phenol sulfide reactant with barium oxide or hydroxide reagent, in the presence of carbon dioxide and water. The instant method, however, involves not a simultaneous neutralization and carbonation as does the method of the British patent, but rather a stepwise addition of metal alcoholate with intermediate carbonation. The distinction between the present method and the prior art method is further evidenced by the following.



(1) The prior art method does not lend itself to the production of complex salts other than barium salts. By the method of the present invention, however, besides the barium salts, complex salts of other metals, such as magnesium and sodium, have been prepared. See Examples 15, 16 and 17, herebelow.

(2) The prior art method requires the presence of water in the neutralization-carbonation of the phenol sulfide for successful operation. In the present method, however, no water is used and none is present in the carbonation step.

(3) The prior art method employs barium hydroxide as the metal reagent, whereas the present method employs a metal alcoholate.

(4) The present method provides a more efficient utilization of barium reagent (alcoholate) than does the prior art method which specifies the use of barium hydroxide, the amount of barium reagent wasted in the present method being about 50% less than in the prior art method. See Examples 4, 5, 7 and 8.

The products of this invention are different from those produced by the prior art method. Thus, (1) the instant products all contain strong base, as shown by their titration curves, whereas the prior art products do not. Also, (2) the products of this invention contain alcoholate substituents, which, of course, are not present in the prior art products.

The present invention, therefore, is seen to provide both a different process and a different complex salt product from those disclosed in the said British patent.

A full understanding of the invention may be had by reference to the following examples illustrating the preparation of various complex carbonated metal phenate sulfides.

*Example 1*

(a) *Nonylphenol sulfide.*—A five liter, four neck, round bottom flask was fitted with a mechanical stirrer, thermometer, dropping funnel and reflux condenser. The initial charge to the flask was 660 grams (3.0 mols) of nonylphenol and 1320 grams, 2 parts by weight, of solvent benzol. To this mixture was added 232 grams (2.25 mols) of sulfur dichloride over a period of 3 hours at 20° C. (cooling required). Hydrogen chloride was evolved. The reaction mass was stirred for one hour at room temperature after the addition was complete. It was then heated at reflux for approximately one hour before take-off of solvent was begun. Solvent was removed by distillation with maximum pot temperature held below 140° C. Nitrogen sweeping and application of vacuum were used to complete the removal of solvent. The product, a highly viscous and tacky material, was diluted at once with 732 grams of process oil (a conventional 100 Sec. at 100° F. paraffin oil). Product weight was 1471 grams. Analysis of nonylphenol sulfide (4:3 mol ratio of phenol OH to $SCl_2$) in oil, one part oil per phenolsulfide resin was as follows:

| | Percent |
|---|---|
| Sulfur | 5.08 |
| Chlorine | 0.64 |

(b) *Complex barium salt.*—Into a five liter, four neck, round bottom flask fitted with a mechanical stirrer, thermometer, dropping funnel and a condenser arranged for take-off of condensate there was charged 1170 grams of the above 1:1 blend of nonylphenol sulfide in process oil together with 1170 grams of additional process oil. This 1:3 blend was calculated to contain 2.39 gram equivalents of phenolic hydroxyl. Barium methylate reagent,

$Ba.OH(OCH_3)$

was added to the mixture at about 90° C. as methanol was removed continuously by distillation. The addition of 1528 grams of reagent of 12.9% barium content (1.2 × 2.39 gram equivalents of barium) required two hours. Nitrogen sweeping was begun and the temperature was raised to 200° C. The nitrogen was replaced by carbon dioxide and carbonation carried out for 3 hours. The reaction mixture was cooled before addition of the second portion of barium methylate. This addition, 1273 grams (1.0 × 2.39 gram equivalents of barium) was also made at 90° C. with continuous distillation of methanol. Addition time was two hours. The temperature was then raised to 150° C. and held there for 1½ hours, using nitrogen sweeping to complete the removal of uncombined methanol. "Hyflo" filter aid (5% by weight) was added and the product fitered through an electrically heated, "Hyflo" precoated, Büchner funnel. The product analyzed as follows:

| | |
|---|---|
| Barium, percent | 11.3 (1.82 eq./eq. phenol OH). |
| Sulfur, percent | 2.15. |
| $CO_2$ (combined), percent | 0.52 (0.26 eq./eq. phenol OH). |
| Chlorine, percent | 0.16. |
| Base No. | 19, 70, 83 [1] |
| Spec. grav. | 1.0373. |
| Vis.: | |
| At 100° F., cs. | 135.9. |
| At 210° F., cs. | 11.75. |
| Copper strip test [2] | Slight tarnish. |

[1] Three "breaks" in titration curve.
[2] SAE 30 conventionally refined Mid-Continent oil+3% product. 24 hour test at 100° C.

*Example 2*

(a) *Nonylphenol sulfide.*—Nonylphenol sulfide was prepared as in Example 1, except that Varnish Maker's and Painter's naphtha (a highly aromatic naphtha) was used as the diluent solvent. After the completion of the reaction and the distillation of the diluent the nonylphenol sulfide was obtained as a resinous solid. The oil-free nonylphenol sulfide product (4:3 mol ratio of phenol to $SCl_2$) analyzed as follows:

| | | |
|---|---|---|
| Sulfur | percent | 10.4 |
| Chlorine | do | 0.95 |
| Molecular wt. | | 720 |

(b) *Complex barium salt.*—The complex barium salt was prepared as in Example 1. In this case the process oil was used in greater amount, 4 parts per part of nonylphenol sulfide instead of 3 parts. The product analysis is given below. For comparison purposes, the calculated values for the 3:1 oil-product salt blend are also given.

TABLE I

| | Found Value 4:1 Oil Product | Calculated Value for 3:1 Oil Product |
|---|---|---|
| Barium, percent | 9.12 (1.77 eq./eq. phenol OH). | 11.15 |
| Sulfur, percent | 1.87 | 2.23 |
| Chlorine, percent | 0.19 | 0.23 |
| Base number | 15, 57, 69 | 18, 70, 83 |

It will be seen that the use of Varnish Maker's and Painter's naphtha in place of benzol in the sulfide preparation and the use of a greater amount of diluent oil in the complex salt preparation does not change the product essentially.

*Example 3*

(a) *Noylphenol sulfide.*—Nonylphenol sulfide was prepared as in Example 1, except that technical white oil was used as diluent in the reaction. Analysis of the nonylphenol sulfide product (4:3 mol ratio of nonylphenol to $SCl_2$) in oil (1:1 weight ratio oil to phenol sulfide) was as follows:

| | Percent |
|---|---|
| Sulfur | 5.02 |
| Chlorine | 0.23 |

(b) *Complex barium salt.*—The complex barium salt was then prepared as in Example 1. The product analyzed as follows:

| | |
|---|---|
| Barium, percent | 11.45 (1.82 eq./eg. phenol OH). |
| Sulfur, percent | 2.48. |
| Base No. | 13, 70, 86. |

It will be seen that the product salt was very similar in analyses to the product of Example 1.

*Example 4*

(a) *Nonylphenol sulfide.*—Nonylphenol sulfide was prepared using no diluent in the initial reaction. The initial charge to the flask was 660 grams (3.0 mols) of nonylphenol. To this was added 232 grams (2¼ mols) of sulfur dichloride over a period of 1¼ hours at 55° C. Hydrogen chloride was evolved. The viscosity was high at the end of the addition. The reaction mixture was heated to 100° C. and blown with nitrogen for 2½ hours. A 50 gram sample was taken and 677 grams of process oil was then added to the remainder to give a 1:1 blend of sulfide in oil (1352 grams recovered). The oil-free product analyzed as follows:

| | | |
|---|---|---|
| Sulfur | percent | 10.2 |
| Chlorine | do | 1.05 |
| Molecular wt. | | 790 |

The 1:1 oil blend of the product showed the following analysis:

| | |
|---|---|
| Viscosity at 210° F., cs. | 13.22 |
| Viscosity at 100° F., cs. | 317.9 |
| N.N. | 18, 69 |

(b) *Complex barium salt.*—The complex barium salt was prepared as follows: The initial charge to the flask was 194 grams of the above 1:1 blend of nonylphenol sulfide in process oil together with 194 grams of additional process oil. This 1:3 blend was calculated to contain 0.4 gram equivalent of phenolic hydroxyl. Barium methylate reagent was added to the oil blend at 80° C. as methanol was removed by distillation. The addition of 374 grams of reagent of 11.77% barium content (1.6×0.4 gram equivalents of barium) required 1½ hours. Nitrogen sweeping was begun and the temperature was raised to 150° C. The nitrogen was replaced by carbon dioxide and carbonation carried out for 3 hours at 150° C. The reaction mixture was cooled before addition of the second portion of barium methylate reagent. This addition, 140 grams (0.6×0.4 gram equivalents of barium) was made at 80–85° C. with continuous distillation of methanol. Addition time was 40 minutes. The temperature was raised to 150° C. and nitrogen blowing continued for one hour to complete the removal of uncombined methanol. "Hyflo" filter aid was added and the product filtered through an electrically heated, "Hyflo" precoated Buchner funnel. The product analysis was as follows:

| | |
|---|---|
| Barium, percent | 12.72 (2.07 eq./eq. phenol OH—94% of theory). |
| Sulfur, percent | 2.18. |
| $CO_2$ (combined), percent | 1.13 (0.57 eq./eq. phenol OH). |
| Base No. | 16, 64, 96. |
| —$OCH_3$, percent | 0.36 (0.13 eq./eq. phenol OH). |

This example illustrates the use of a sulfide intermediate prepared in the absence of any diluent. Also, the high metal content attained by the use of a 1.6 metal

equivalent charge in the pre-carbonation step and a 0.6 metal equivalent charge in the post-carbonation step is apparent.

*Example 5*

For purpose of comparison, a carbonated barium nonylphenate sulfide was prepared by the method disclosed in Example 1 of British Patent No. 744,942.

In this example, 2.2 gram equivalents of barium hydroxide octahydrate were charged per gram equivalent of phenolic hydroxyl. This is the same amount of barium charged in Example 4 (above).

A three liter, four neck, round bottom flask was fitted with a mechanical stirrer, thermometer, gas inlet and a condenser arranged for take-off of condensate. To this flask was charged 488 grams of nonylphenol sulfide (approximately 1.0 gram equivalent of phenolic hydroxyl) prepared as in Example 4 and containing 50% process oil, 160 grams of additional process oil and 27 grams of Lorol 5. (Lorol 5 is a mixture of $C_{10}$–$C_{18}$ alcohols having an average molecular weight of about 200.) The composition of the charge was thus 36% nonylphenol sulfide resin, 60% process oil and 4% Lorol 5. To this mixture was added 347 grams of barium hydroxide octahydrate (2.2 gram equivalents of barium). The contents of the flask were heated to 120° C., then steam was introduced through the gas inlet. After one hour of steaming at 120° C., the steam was replaced by carbon dioxide which was humidified by bubbling through water. Carbonation was carried out for two hours at 120° C. The temperature was then raised to 150° C., "Hyflo" filter aid was added and the product filtered through a "Hyflo" precoat on an electrically heated Buchner funnel. The product analysis was as follows:

| | |
|---|---|
| Barium, percent | 16.3 (1.91 eq./eq. phenol OH—87% of theory). |
| $CO_2$ (combined), percent | 3.38 (1.24 eq./eq. phenol OH). |
| Sulfur, percent | 2.65. |
| Base No. | 54, 111. |

This example, compared with Example 4, shows the procedure of this invention to provide over 50% less waste of barium reagent than the steam-wet $CO_2$ procedure of the British patent, i.e., 6% vs. 13%.

*Example 6*

A complex carbonated barium nonylphenate sulfide was prepared from the nonylphenol sulfide of Example 1.

The reaction was carried out as in Example 1, with the sole exception that the first addition of barium methylate reagent contained only 1.0, rather than 1.2, gram equivalents of barium per phenolic hydroxyl. The product analyzed as follows:

| | |
|---|---|
| Barium, percent | 10.1 (1.6 eq./eq. phenol OH). |
| $CO_2$ (combined), percent | 0.43 (0.21 eq./eq. phenol OH). |
| Base No. | 19, 73. |

This example shows the lower metal and $CO_2$ content of a product prepared without excess metal in the first addition. (Cf. Examples 1 to 4.)

*Example 7*

(a) *Nonylphenol sulfide.*—A five liter, four neck, round bottom flask was fitted with a mechanical stirrer, thermometer, dropping funnel and reflux condenser. The initial charge to the flask was 880 grams (4.0 mols) of nonylphenol and 1760 grams (2 parts by weight) of benzene. To this mixture was added 309 grams (3.0 mols) of sulfur dichloride over a period of one hour at 18–25° C. (cooling required). Hydrogen chloride was evolved. The reaction mass was then heated to distill off solvent. Application of vacuum at the maximum temperature of 140° C. was used to complete the removal of solvent. The product, a highly viscous and tacky material, was diluted at once with 976 grams of mineral oil. Product weight was 1955 grams. Analysis of nonylphenol sulfide (4:3 mol ratio of phenol sulfide to $SCl_2$) in oil, one part oil per phenol sulfide, was as follows:

| | Percent |
|---|---|
| Sulfur | 5.04 |
| Chlorine | 0.88 |

(b) *Complex barium salt.*—A four neck, round bottom flask was fitted with a mechanical stirrer, a thermometer, dropping funnel and a condenser arranged for take-off of condensate. The initial charge to the flask was 488 grams of the 1:1 blend of nonylphenol sulfide in mineral oil together with 488 grams of additional mineral oil. This 1:3 blend was calculated to contain 1.0 gram equivalent of phenolic hydroxyl. Barium methylate reagent was added to the oil blend at 75–85° C. as methanol was removed continuously by distillation. The addition of 850 grams of reagent of 12.9% barium content (1.6×1.0 gram equivalents) required two hours. Nitrogen sweeping was begun and the temperature was raised to 190° C. The nitrogen was replaced by carbon dioxide and carbonation continued for 3 hours at 190–200° C. The reaction mixture was cooled before addition of the second portion of barium methylate reagent. This addition, 425 grams (0.8×1.0 gram equivalent) was made at about 80° C. with continuous distillation of methanol. Addition time was one hour. The reaction mixture was heated to 190° C. under nitrogen, then treated with $CO_2$ for 3 hours at 190–200° C. It was treated again with barium methylate reagent, 425 grams (0.8×1.0 gram equivalent) added in one hour at 85° C. The temperature was raised to 150° C. and vacuum applied to complete the removal of unreacted methanol. "Hyflo" filter aid was added and the product filtered through an electrically heated, "Hyflo" precoated, Buchner funnel. The product analyzed as follows:

| | |
|---|---|
| Barium, percent | 16.2 (2.79 eq./eq. phenol OH—87% of theory). |
| Sulfur, percent | 2.0. |
| $CO_2$ (combined), percent | 2.06 (1.11 eq./eq. phenol OH). |
| Base No. | 29, 66, 116. |
| Vis. at 210° F., cs. | 24.53. |
| Cu strip test [1] | Pass. |

[1] SAE 30, conventionally refined, Mid-Continent oil+2% product. 24 hour test at 100° C.

This example is illustrative of the high metal content attainable when carbonation and barium methylate reagent addition are used repeatedly.

*Example 8*

For purpose of comparison, a carbonated barium nonylphenate sulfide was prepared by the method of Example 1 of British Patent No. 744,942. In this example 3.2 gram equivalents of barium hydroxide octahydrate were charged per gram equivalent of phenolic hydroxyl. This is the same amount of barium charged in Example 7 (above).

A mixture of 488 grams of nonylphenol sulfide (approximately 1.0 gram equivalent of phenolic hydroxyl) containing 50% process oil, 160 grams of additional process oil and 27 grams of Lorol 5 were reacted with 504 grams of barium hydroxide octahydrate (3.2 gram equivalents) by the procedure used in Example 5. The product analyzed as follows:

| | |
|---|---|
| Barium, percent | 20.8 (2.56 eq./eq. phenol OH—80% of theory). |
| $CO_2$ (combined), percent | 5.2 (1.99 eq./eq. phenol OH). |
| Sulfur, percent | 2.37. |
| Base No. | 40, 140. |

This example, compared with Example 7, shows the steam-wet $CO_2$ procedure to give poorer utilization of barium, i.e., 80% vs. 87% for Example 7. Expressed differently, the waste of barium reagent in the instant process is only 13% as compared to 20% for the prior art method.

*Example 9*

A 100-gram sample of the product of Example 7 (taken before filtration) was heated to 190° C. under a stream of nitrogen. The nitrogen was then replaced by carbon dioxide and carbonation carried out for 1½ hours at 190–200° C. Fifty grams of the unfiltered product (approximately 0.04 gram equivalent of phenolic hydroxyl) was diluted with an equal weight of mineral oil. This blend was treated with barium methylate reagent containing 12.9% barium. The addition of 17 grams of reagent (0.8×0.04 gram equivalents) was carried out in 20 minutes, at about 85° C., with continuous distillation of methanol. The temperature was then raised to 150° C. with nitrogen sweeping and vacuum applied to complete the removal of uncombined methanol. "Hyflo" filter aid was added and the product filtered through a "Hyflo" precoated on an electrically heated Buchner funnel. The product analysis was as follows:

| | |
|---|---|
| Barium, percent | 9.9 (3.6 eq./eq. phenol OH). |
| Base No. | 34, 73. |
| Cu strip test [1] | Pass. |

[1] SAE 30, conventionally refined, Mid-Continent oil+4% product. 24 hour test at 100° C.

It will be observed that the additional $CO_2$ and barium methylate treatment still further increased the complexed metal over that of Example 7.

*Example 10*

Carbonation at relatively low temperature has been practiced successfully. A nonylphenol sulfide (4.3 mol ratio nonylphenol:$SCl_2$) was reacted with barium methylate reagent as in Example 1. However, the carbonation period was 2 hours and 25 minutes and the temperature of carbonation was only 150° C. The product analysis was as follows:

| | |
|---|---|
| Barium, percent | 11.6 (1.87 eq./eq. phenol OH). |
| Sulfur, percent | 2.23. |
| $CO_2$ (combined), percent | 0.75 (0.38 eq./eq. phenol OH). |
| Base No. | 12, 95. |
| —$OCH_3$, percent | 0.38 (0.14 eq./eq. phenol OH). |

This example shows that $CO_2$ is effectively combined in the product at a temperature below that used in the previous examples. The lower carbonation temperature also results in a lighter-colored product.

*Example 11*

Dodecylphenol was used to prepare a sulfide intermediate after the fashion of Example 1. Analysis of the product, one part mineral oil per part phenol sulfide, was as follows:

| | Percent |
|---|---|
| Sulfur | 4.33 |
| Chlorine | 0.28 |

The complex barium salt was prepared as in Example 4. The product analyzed as follows:

| | |
|---|---|
| Barium, percent | 10.71 (2.01 eq./eq. phenol OH). |
| Base No. | 10, 57, 78. |
| $CO_2$, percent | 1.18 (0.69 eq./eq. phenol OH). |
| Sulfur, percent | 1.95. |



*Example 12*

Diamylphenol (3 mols) was diluted with Varnish Maker's and Painter's naphtha and reacted with sulfur dichloride (2¼ mols) after the fashion of Example 1. Analysis of the diamylphenol sulfide product (oil free) was as follows:

| | Percent |
|---|---|
| Sulfur | 11.3 |
| Chlorine | 1.23 |

This intermediate was converted to the carbonated complex barium salt by the procedure of Example 1. The product analyzed as follows:

TABLE II

| | Found Value, 4:1 Oil Product | Calc. Value For 3:1 Oil Product |
|---|---|---|
| Barium, percent | 9.0 (1.84 eq./eq. phenol OH). | 11.0. |
| Sulfur, percent | 1.86. | 2.33. |
| Base number | 23, 36, 64. | 28, 45, 78 |

*Example 13*

A dinonylphenol sulfide (2:1 mol ratio of the phenol to sulfur dichloride) was treated with several additions of barium methylate reagent and $CO_2$ according to the procedure given in Example 7. The product analyzed as follows:

| | |
|---|---|
| Barium, percent | 12.4 (3.05 eq./eq. phenol OH). |
| Sulfur, percent | 1.05. |
| $CO_2$ (combined), percent | 2.25 (1.72 eq./eq. phenol OH). |
| Base No. | 34, 89. |

The dilution effect of the two substituent alkyl groups accounts for the low metal content as compared with Example 7.

*Example 14*

Dinonylphenol (3.0 mols) was diluted with benzol and reacted with sulfur dichloride (3.0 mols) as in Example 1. Analysis of the dinonylphenol sulfide 1:1 oil blend was as follows:

| | Percent |
|---|---|
| Sulfur | 4.21 |
| Chlorine | 1.95 |

This intermediate was treated with several additions of barium methylate and $CO_2$ according to the procedure given in Example 7. Analysis of the carbonated complex barium salt was as follows:

| | |
|---|---|
| Barium, percent | 12.0 (2.99 eq./eq. phenol OH). |
| Sulfur, percent | 1.41. |
| Base No. | 21, 71. |

*Example 15*

A complexed magnesium nonylphenate sulfide was prepared by essentially the same procedure used for the barium salts. A three liter, four neck, round bottom flask was fitted with a mechanical stirrer, thermometer, dropping funnel, nitrogen inlet, and a condenser arranged for take-off of condensate. To this flask was charged 244 grams of nonylphenol sulfide (calculated to contain 1.0 gram equivalent of phenolic hydroxyl) and 732 grams of process oil. A solution of magnesium methylate prepared from 14.6 grams of magnesium turnings (1.2 gram equivalents) and 250 milliliters of methanol was added over a 1 hour period at about 80° C., with simultaneous distillation of methanol. Nitrogen sweeping was begun and the temperature raised to 190° C. The nitrogen was replaced by carbon dioxide and carbonation continued for three hours at 190–200° C. The reaction mixture

was cooled to 75° C. and a second charge of magnesium methylate, prepared from 12.2 grams of magnesium (1.0 gram equivalent) and 200 milliliters of methanol, added in 1 hour. The temperature was raised to 150° C. with nitrogen sweeping and vacuum applied to complete the removal of uncombined methanol. Another 244 grams of process oil was then added to increase the fluidity of the product. "Hyflo" filter aid was added and the product filtered through a "Hyflo" precoat on an electrically heated Buchner funnel. The product analyzed as follows:

Magnesium, percent ..... 1.68 (1.72 eq./eq. phenol OH).
Sodium, percent ..... 2.10.
$CO_2$ (combined), percent .. 0.47 (0.27 eq./eq. phenol OH).

It will be seen that this example is comparable to Example 1 in method, reagent ratios and product analysis.

*Example 16*

A complex carbonated sodium phenate sulfide was prepared by essentially the same procedure used for the barium salts.

A two liter, four neck, round bottom flask was fitted with a mechanical stirrer, thermometer, nitrogen inlet and a condenser arranged for take-off of condensate. Sodium methylate was prepared in this flask by adding 18.4 grams of metallic sodium (0.8 gram equivalent) to 300 milliliters absolute methanol. To this reagent were added 122 grams of nonylphenol sulfide (calculated to contain 0.5 gram equivalent of phenolic hydroxyl) and 366 grams of process oil. (The nonylphenol sulfide was prepared with a 4:3 nonylphenol:sulfur dichloride mol ratio. It was found to contain 10.6% S and 1.02% Cl.) The reaction mixture was heated to methanol reflux, refluxed to ½ hour, methanol distilled in 1 hour and the temperature raised to 190° C. with nitrogen sweeping. The nitrogen was then replaced with carbon dioxide and carbonation carried out for 2½ hours at 190–200° C.

A solution of sodium methylate was prepared from 6.9 grams of metallic sodium (approximately 0.3 gram equivalent) and 200 milliliters of absolute methanol. This solution was added to the above carbonated product at room temperature. The mixture was then heated to methanol reflux, refluxed for ½ hour, methanol distilled in ½ hour and the temperature raised to 150° C. with nitrogen sweeping and application of vacuum. "Hyflo" filter aid was added and the product filtered through a "Hyflo" precoat on an electrically heated Buchner funnel. The product analyzed as follows:

Sodium, percent ..... 4.3 (1.91 eq./eq. phenol OH).
$CO_2$ (combined), percent .. 1.60 (0.40 eq./eq. phenol OH).
Base No. ..... 59, 85, 107.

*Example 17*

A complex carbonated sodium phenate sulfide was prepared with carbonation at 125° C. The nonylphenol sulfide used was prepared from a 4:3 mol ratio of nonylphenol and $SCl_2$. Diluted with an equal part of process oil it contained 5.25% S and 0.38% Cl. The complex carbonated sodium phenate sulfide was prepared as in Example 16, except that carbonation was carried out at 125° C. instead of 200° C. The product analyzed as follows:

Sodium, percent ..... 3.42 (1.5 g. eq./g. eq. phenol OH).
$CO_2$ (combined), percent .. 0.97.
Base No. ..... 27, 68, 78.

It is seen that the degree of complexing is lower than in Example 16 due to the lower carbonation temperature.

*Example 18*

Barium hydroxide octahydrate was substituted for barium methylate in preparing the complex carbonated barium nonylphenate sulfide.

Into a flask reactor of the same type used in the previous examples there was placed 244.4 grams of nonylphenol sulfide prepared as in Example 5 and containing 50% process oil. Its analysis showed 5.25% S and 0.38% Cl. To the nonylphenol sulfide were added another 244 grams of process oil and 129 grams of barium hydroxide octahydrate (assay 98%) (1.6×0.5 gram equivalents).

This mixture was heated to 200° C. in 3½ hours, a stream of nitrogen being used to help carry off the water. After cooling to 150° C. the nitrogen was replaced by carbon dioxide and carbonation carried out for 2½ hours at 145–155° C. The reaction mixture was then cooled to room temperature and 48 grams of barium hydroxide octahydrate (0.6×0.5 gram equivalents) added. Dehydration to 200° C. was accomplished in 2 hours. The cooled product was mixed with "Hyflo" filter aid and filtered through a "Hyflo" precoat on an electrically heated Buchner funnel. The product analysis was as follows:

Barium, percent ..... 10.8 (1.73 eq./eq. phenol OH—81% of theory).
Base No. ..... 7, 69.
$CO_2$ (combined), percent ... 0.97.

It is seen that this product contains less barium then the comparable product from barium methylate (Example 4). (2.07 vs. 1.73 eq. Ba/phenol OH.)

*Example 19*

Addition of barium reagent to nonylphenol sulfide without carbonation produces a salt having a low degree of complexing.

One hundred grams of nonylphenol sulfide (4:3 mol ratio nonylphenol to $SCl_2$) (0.207 gram equivalent of phenolic hydroxyl), prepared as in Example 2 and containing 50% mineral oil, was further diluted with 100 grams of mineral oil. This blend was treated with barium methylate reagent containing 12.2% barium. The addition of 256 grams of this reagent (2.2×0.207 gram equivalents) was carried out in 1½ hours, at 75–90° C., with continuous distillation of methanol. The temperature was then raised to 150° C. with nitrogen sweeping and vacuum applied to complete the removal of uncombined methanol. "Hyflo" filter aid was added and the product filtered through an electrically heated Buchner funnel precoated with "Hyflo." The product analyzed as follows:

Barium, percent .....8.6 (1.34 eq./eq. phenol OH)

This example shows that adding the optimal 2.2 gram equivalents of barium, without carbonation, produces a salt with less than half of the complexed barium found in Examples 1 to 4.

*Example 20*

The addition of 2.2 gram equivalents of barium reagent to nonylphenol sulfide followed by carbonation produces a salt having a relatively low degree of complexing.

Two hundred and forty grams of nonylphenol sulfide (4:3 mol ratio nonylphenol to $SCl_2$) (approximately 0.5 gram equivalent of phenolic hydroxyl), prepared as in Example 2 and containing 50% mineral oil, was further diluted with 240 grams of mineral oil. This blend was treated with barium methylate reagent containing 12.2% barium. The addition of 618 grams of this reagent (2.2×0.5 gram equivalents) was carried out in 1½ hours at 80–90° C., with continuous distillation of methanol. The temperature was then raised to 190° C. with nitrogen sweeping. The nitrogen was replaced by

$CO_2$ and carbonation continued for 5 hours at 190–200° C. "Hyflo" filter aid was added and the product filtered through a "Hyflo" precoat on an electrically heated Buchner funnel. The product analyzed as follows:

Barium, percent ---------- 9.1 (1.42 g. eq./eq. phenol OH—65% of theory).
$CO_2$ (combined), percent ---- 1.33 (0.33 eq./eq. phenol OH).
Base No. ---------- 49, 72.

It is seen that the product salt contained only about half of the complexed barium found in Examples 1, 2 and 3.

*Example 21*

Three and two-tenths gram equivalents of barium reagent were added to nonylphenol sulfide all at once with final carbonation.

Two hundred and fifty grams of a 1:1 oil blend of a nonylphenol sulfide (0.5 gram equivalent of phenolic hydroxyl) prepared by reaction of 3 mols of nonylphenol with 3 mols of sulfur dichloride after the fashion of Example 1 was further diluted with 250 grams of process oil. This blend was treated with barium methylate reagent containing 12.9% barium. The addition of 855 grams of this reagent (3.2×0.5 gram equivalents) was carried out in 2 hours at 80–90° C. with continuous distillation of methanol. The temperature was then raised to 190° C. with nitrogen sweeping. The nitrogen was replaced by $CO_2$ and carbonation continued for 2½ hours at 190–200° C. "Hyflo" filter aid was added and the product filtered through a "Hyflo" precoat on an electrically heated Buchner funnel. The product analyzed as follows:

Barium, percent ------ 9.7 (1.57 g. eq./eq. phenol OH).
Base No. ---------- 33, 67.

It is seen that adding 3.2 gram equivalents of barium at one time gives a product with much less complexed barium than found with the step-wise procedure.

To establish whether or not a Kolbe type reaction, resulting in carboxylation of the phenol rings, takes place under the reaction conditions used in preparing the products of the invention, the following examples (22 and 23) were carried out. In each case, the basic salt was rendered metal-free by treatment with mineral acid. The de-metallized material was then inspected by infra-red analysis and potentiometric titration for the presence of carboxylic acid.

*Example 22*

A complex carbonated barium nonylphenate sulfide (carbonated at 200° C.) was de-metallized by treatment with acid as follows: A 50-gram portion of the complex salt product of Example 1 was stirred for 15 minutes with a mixture of 25 milliliters of concentrated HCl and 25 milliliters of distilled water. One hundred milliliters of distilled water and 10 milliliters of n-butanol were then added, the mixture shaken, and the aqueous layer drawn off. After two more acid treats the oil layer was washed free of HCl. The washings were extracted with three 50 milliliter portions of benzene. The benzene extract and oil layer were then combined, filtered through paper and the benzene distilled. The product analyzed as follows:

Acid No. ---------- 12 (no break).
Infra-red analysis -- The infra-red spectrum shows no absorption due to the carboxyl group.
Oxygen, percent --- 1.38 (theory for nonylphenol sulfide with 3 parts of oil is 1.32%).

This example shows that $CO_2$ treatment of a barium nonylphenate sulfide at 200° C. does not result in carboxylation. The weak acid number found is due to the hyperacidity of the phenolic groups in the nonylphenol sulfide.

*Example 23*

A complex carbonated barium nonylphenate sulfide (carbonated at 150° C.) was de-metallized with acid as follows: A 20-gram portion of the product of Example 4 was dissolved in 100 milliliters of chloroform. This solution was shaken vigorously with a mixture of 50 milliliters of concentrated HCl and 50 milliliters of distilled water. One hundred milliliters of acetone were added and the mixture shaken again. After adding another 100 milliliters of chloroform, the aqueous layer was drawn off. The chloroform layer was filtered through paper and the chloroform distilled. The product analyzed as follows:

Acid number ---- 16 (no break).
Infra-red analysis -- The infra-red spectrum shows no absorption due to the carbonyl group.

This example shows that $CO_2$ treatment of a barium nonylphenate sulfide at 150° C. does not result in carboxylation. Again, the weak acid number found is due to the hyperacidity of the phenolic groups in the nonylphenol sulfide.

## EVALUATION OF COMPLEX SALTS AS LUBRICATING OIL ADDITIVES

The ability of the complex carbonated metal alkyl phenol sulfide salts herein contemplated as lubricating oil additives has been shown by a number of comparative tests conducted on base lubricating oils alone and these same oils blended with minor amounts of representative product salts described in the preceding examples. The test procedures employed and the results obtained were as follows:

(a) *Laboratory detergency test.*—The test shows the effectiveness of detergent additives in automotive lubricating oils. In this test a heated aluminum cylinder 1 inch in diameter and 6⅛ inches in length is dipped once each minute for 10 seconds into 660 milliliters of test oil maintained at 250° F. by a constant temperature bath. In the remaining 50 seconds of each cycle the thin film of oil on the heated aluminum cylinder is allowed to oxidize in air maintained as free of drafts as possible. The aluminum cylinder is maintained at an average temperature of 480° F. by an electric heater within its heavy walls. After 16 hours, the cylinder is allowed to cool, wiped free of loose deposits and washed with naphtha. The cylinder is rated by comparison with a set of standards. Ratings are given from 0 through 5. Oils giving the cleanest cylinder are given the lowest ratings, a rating of zero indicating a perfectly clean cylinder. Oils giving ratings of 3 or less would be expected to be good engine oil detergents.

(b) *Catalytic oxidation test.*—This test determines the effectiveness of an additive in preventing catalytic oxidation of an oil. The test procedure is as follows. In a 200 x 25 mm. test tube is placed a 25 cc. sample of test oil having immersed therein (*a*) 15.6 sq. in. of sand-blasted iron wire, (*b*) 0.78 sq. in. of polished copper wire, (*c*) 0.87 sq. in. of polished aluminum wire and (*d*) 0.167 sq. in. of polished lead surface. The oil is heated to a temperature of 260° F. and maintained at this temperature, while dry air is being passed therethrough, at a rate of 18 liters per hour, for 40 hours. The results of the test are reported in terms of stability number of the additive. The stability number is the percentage of additive (in the oil) multiplied by 100, that reduces the N.N. (Neutralization Number) of the reference oil to a value of 2. Thus, the lower the additive stability number, the more effective the additive and vice versa. A stability number of 100 or less signifies a very good antioxidant.

(c) *Caterpillar engine test.*—This test determines the ability of an oil to prevent piston deposits and top ring

wear. A single cylinder, 4-cycle Caterpillar engine is used. The operating conditions are as follows:

| | | |
|---|---|---|
| Oil temperature | ° F. | 150 |
| Jacket temperature | ° F. | 180 |
| Speed | r.p.m. | 1000 |
| Brake load | H.P. | 19.8 |

The duration of the test is 120 hours. The amount of piston deposits at the end of the test is expressed by a piston cleanliness rating based on a scale of from 0 to 100, a rating of 100 signifying a perfectly clean piston. The diesel fuel used in the tests contained 0.4% of sulfur.

The results obtained in the Laboratory Detergency Test (L.D.T.) and in the Catalytic Oxidation Test (C.O.T.) are presented in Table III. It will be seen from the test data that the products of the invention are excellent detergents in all cases and generally are good antioxidants.

The results obtained in the Caterpillar Engine Test are given in Table IV.

TABLE III

| Additive Ex. No. | Percent Barium | L.D.T. Test Rating [1] | C.O.T. Test Stability No.[2] |
|---|---|---|---|
| None | 0 | 4 | |
| 1 | 11.3 | | <25 |
| 2 | 9.12 | | <50 |
| 3 | 11.45 | | 65 |
| 4 | 12.72 | 3 | 32 |
| 7 | 16.2 | 2 | 30 |
| 9 | 9.9 | | |
| 10 | 11.6 | 3 | 37 |
| 11 | 10.7 | 1 | 32 |
| 12 | 9.0 | | >100 |
| 13 | 12.4 | 2 | >100 |
| 14 | 12.0 | 2 | >100 |
| 15 | (Mg) 1.68 | 0 | |
| 16 | (Na) 4.3 | | 17 |

[1] Additives were blended to give 0.3% barium, or equivalent, in an SAE 30, solvent refined, Mid-Continent base oil.
[2] In an SAE 20, solvent refined, Pennsylvania oil.

TABLE IV.—CATERPILLAR TESTS

| Additive Used | Concentration, Percent | Piston Rating |
|---|---|---|
| None [1] | 0 | 61.9 |
| Example 1 [2, 3] | 2.5 | 98.4 |

[1] The base oil was an SAE 30, conventionally-refined, Mid-Continent oil.
[2] A repeat preparation of Example 1.
[3] The additive was blended to give 0.3% barium in oil.

From the high piston rating obtained as shown in Table IV, it is evident that the complex salt products of the invention are excellent detergents for engine lubricating oils.

## EVALUATION OF COMPLEX SALTS AS FUEL ADDITIVES

(a) *Anti-rust test.*—To demonstrate the ability of the products of this invention as rust inhibitors in gasoline, a complex salt product prepared after the fashion of Example 2, hereinabove, and containing 8.43% barium, was subjected to the A.S.T.M. D 665–47–T test. The conditions of this test are recognized as being much more severe than actual pipeline conditions in that much more water is present and it is generally accepted that test specimens exposed to the severe rusting conditions of this test for 48 hours are rusted to substantially the same degree as those exposed to a products pipeline for 30 to 60 days. Briefly, the test involves immersing a cylindrical steel specimen in a mixture consisting of 300 milliliters of the test gasoline and 30 milliliters of water and maintaining the temperature of the mixture at 140° F. while stirring the mixture for 48 hours. The specimen is then withdrawn and examined to determine whether or not it has rusted.

As is well known in the art, an important limitation on the use of rust-preventatives in gasoline is the effect thereof on gum formation. As a generalization, it can be said that most rust-preventatives are non-volatile in nature and increase the amount of gum formed by the amount of preventative added. Consequently, a rust preventative useful in gasoline must be effective in concentrations no greater than about 0.008 weight percent non-volatile residue.

The A.S.T.M. test was conducted using a base gasoline comprised of 40% thermally cracked component, 40% catalytically cracked component and 20% straight-run component and having a boiling range of approximately 100–400° F. While the base (uninhibited) gasoline failed the test, the base gasoline having blended therewith 0.0025 weight percent of the complex carbonated barium phenol sulfide salt successfully passed the test.

(b) *Anti-sludging test.*—The ability of the products of the invention as sediment inhibitors in stored fuel oils has been demonstrated by a series of storage tests conducted on a base fuel oil and blends thereof with the same complex barium salt product (8.43% barium) prepared after the fashion of the product of Example 2 (supra). The base fuel oil used comprised a blend of 60% catalytically cracked component and 40% straight-run component and had a boiling range of approximately 320–640° F. The test used was the 110° F. storage test. In this test a 500 milliliter sample of the fuel oil under test is placed in a convected oven maintained at 110° F. for a period of 12 weeks. The sample is then removed from the oven and cooled. The cooled sample is filtered through a tared asbestos filter (Gooch crucible) to remove the insoluble matter. The weight of such matter, in milligrams, is reported as the amount of sediment. The effectiveness of an additive as a sediment inhibitor is determined by comparing the test data for the inhibited fuel oil with that of the uninhibited fuel oil. The test results are given in Table V.

TABLE V.—TWELVE WEEKS STORAGE AT 110° F.

| Inhibitor | Concentration, lbs./1,000 bbls. | Sediment, mg./liter |
|---|---|---|
| None | 0 | 80 |
| Example 2 type product | 25 | 10 |
| Do | 50 | 7 |
| Do | 100 | 7 |

It will be seen from the test data that the complex metal phenol sulfide salt product effectively stabilizes the fuel oil against sediment formation in storage.

(c) *Anti-screen clogging test.*—The ability of the complex salts of the invention as anti-screen clogging agents has been demonstrated by a series of tests conducted on a base fuel oil and blends of the base oil with the same Example 2 type product used in the aforedescribed storage tests. The base oil was also the same as that used in the storage tests. The test procedure was as follows: The test is conducted with a Sundstrand V3 or S1 home fuel oil burner pump with a self contained 100 mesh Monel metal screen. About 0.05%, by weight, of naturally formed fuel oil sediment, composed of fuel oil, water, dirt, rust and organic sludge is mixed with 10 liters of the fuel oil. This mixture is circulated by the pump through the screen for 6 hours. The sludge deposit on the screen is washed off with normal pentane and filtered through a Gooch crucible. After drying, the Gooch crucible is washed with a 50–50 acetone-methanol mixture. The total organic sediment is obtained by evaporating the pentane and acetone-methanol filtrates. Drying and weighing the Gooch crucible yields the inorganic sediment. The sum of the organic plus inorganic deposits on the screen may be reported in milligrams or converted to percent of screen clogging. The test results are presented in Table VI.

TABLE VI.—SCREEN-CLOGGING TEST

| Inhibitor | Concentration, lbs./1,000 bbls. | Screen-Clogging, Percent |
|---|---|---|
| None | 0 | 100 |
| Example 2 type product | 25 | 38 |
| Do | 50 | 23 |
| Do | 100 | 29 |

It will be seen from the data that the product of the invention is an effective anti-clogging agent for use in fuel oil.

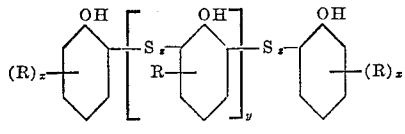
It will be appreciated that the products as provided by the process of this invention are ordinarily concentrated oil solutions of the complex carbonated metal phenate sulfide salts, these solutions containing from about 30% to about 70%, by weight, of the complex salts, the particular concentration depending upon the process conditions employed, including the amount of solvent oil used in the process, etc. The amount of the products which is added to a petroleum fraction to provide a particular concentration of complex salt therein will, therefore, vary somewhat with a particular product. As a practical matter, however, differences in the products can be readily eliminated by standardization of process conditions and/or final adjustment of the product oil solutions to some standard salt content as will be readily appreciated by those skilled in the art. Allowing for the usual variations in the salt contents of the product oil solutions, i.e., from about 30% up to about 70% of complex salt content, the amounts of the products to be utilized as detergents in lubricating oil will range broadly from about 0.5% to about 20%, by weight, the usual amount being from about 2% to about 8%. On the other hand, when the products are used as anti-rust agents in gasoline, the amounts employed may range from about 0.0003% to about 0.008% by weight. Correspondingly, when utilized as fuel oil additives, the amounts of the products to be employed will range from about 10 to about 200 pounds per 1000 barrels of fuel oil, i.e., from about 0.003% to about 0.06% by weight.

The various compositions of the invention, i.e., lubricating oils, fuel oils and gasolines, may contain other addition agents along with the complex salt products disclosed herein. Thus, for example, the lubricating oil compositions may contain pour point depressants, viscosity index improvers, extreme pressure agents, additional detergents, etc., while the fuel oils may contain demulsifiers, ignition improvers and the like. Likewise, the gasoline compositions may contain anti-knock agents, pre-ignition additives, antioxidants, metal-deactivators, dyes, anti-stall additives, etc.

Although the present invention has been described herein by means of certain specific embodiments and illustrative examples, it is not intended that the scope thereof be limited in any way thereby, but only as indicated in the following claims.

What is claimed is:

1. A process for producing a complex carbonated metal phenate sulfide salt which comprises the following sequence of steps: (1) interacting a hydrocarbon solution of an alkyl phenol sulfide of the general formula:



wherein R represents an alkyl radical having from about 5 to about 24 carbon atoms, $x$ represents an integer from 1 to 4, $y$ represents an integer from 0 to 3 and $z$ represents an integer from 1 to 5, with a metal alcoholate having the formula selected from the group consisting of Ba.OH(OR), NaOR and $Mg(OR)_2$, where R in all instances represents an alkyl radical of from 1 to 4 carbon atoms, in a proportion to supply to the reaction from at least about 1.2 to about 1.6 equivalents of metal per equivalent of phenol hydroxyl supplied by the phenol sulfide reactant, at a temperature of from about 80° C. to about 150° C., (2) increasing the temperature of the reaction mixture to from about 125° C. to about 200° C., (3) intimately contacting the reaction mixture at this latter temperature with carbon dioxide in sufficient amount and for a sufficient time to incorporate in the complex salt product from at least about 0.2 to at least about 0.6 equivalent of carbon dioxide based on the equivalents of phenol hydroxyl combined in said product, (4) lowering the temperature of the reaction mixture to from about 80° C. to about 150° C., (5) interacting the reaction mixture at this latter temperature with additional metal alcoholate in an amount to supply to the reaction from about 0.6 to about 1.0 equivalent of metal per equivalent of phenol hydroxyl originally supplied by the alkyl phenol sulfide reactant, (6) again raising the temperature of the reaction mixture to a level of from about 125° C. to about 200° C. and (7) filtering the reaction mixture to recover a hydrocarbon solution of the complex carbonated metal phenate sulfide salt.

2. The process according to claim 1 wherein the reaction mixture from step 6 is subjected to further carbonation and further reaction with metal alcoholate as recited in steps 3 to 6, inclusive, to incorporate additional carbon dioxide and metal in the complex salt.

3. A process for producing a complex carbonated barium phenate sulfide salt which comprises the following sequence of steps: (1) interacting a hydrocarbon solution of a diamyl phenol sulfide, prepared by the reaction of about 4 mol proportions of diamyl phenol with 3 mol proportions of sulfur dichloride, with barium methylate in a proportion to supply to the reaction from at least about 1.2 to about 1.6 equivalents of barium per equivalent of phenol hydroxyl supplied by the phenol sulfide reactant, at a temperature of from about 80° C. to about 150° C., (2) increasing the temperature of the reaction mixture to from about 125° C. to about 200° C., (3) intimately contacting the reaction mixture at said latter temperature with carbon dioxide in sufficient amount and for a sufficient time to incorporate in the complex salt product from at least about 0.2 to at least about 0.6 equivalent of carbon dioxide per equivalent of phenol hydroxyl combined in said product, (4) lowering the temperature of the reaction mixture to from about 80° C. to about 150° C., (5) interacting the reaction mixture at said latter temperature with additional barium alcoholate in an amount to supply to the reaction from about 0.6 to about 1.0 equivalent of barium per equivalent of phenol hydroxyl originally supplied by the alkyl phenol sulfide reactant, (6) again raising the temperature of the reaction mixture to a level of from about 125° C. to about 200° C. and (7) filtering the reaction mixture to recover a hydrocarbon solution of the complex carbonated barium phenate sulfide salt.

4. A process for producing a complex carbonated barium phenate sulfide salt which comprises the following sequence of steps: (1) interacting a hydrocarbon solution of a dodecyl phenol sulfide, prepared by the reaction of about 4 mol proportions of dodecyl phenol with 3 mol proportions of sulfur dichloride, with barium methylate in a proportion to supply to the reaction from at least about 1.2 to about 1.6 equivalents of barium per equivalent of phenol hydroxyl supplied by the phenol sulfide reactant, at a temperature of from about 80° C. to about 150° C., (2) increasing the temperature of the reaction mixture to from about 125° C. to about 200° C., (3) intimately contacting the reaction mixture at said latter temperature with carbon dioxide in sufficient amount and for a sufficient time to incorporate in the complex salt product from at least about 0.2 to at least about 0.6 equivalent of carbon dioxide

per equivalent of phenol hydroxyl combined in said product, (4) lowering the temperature of the reaction mixture to from about 80° C. to about 150° C., (5) interacting the reaction mixture at said latter temperature with additional barium alcoholate in an amount to supply to the reaction from about 0.6 to about 1.0 equivalent of barium per equivalent of phenol hydroxyl originally supplied by the alkyl phenol sulfide reactant, (6) again raising the temperature of the reaction mixture to a level of from about 125° C. to about 200° C. and (7) filtering the reaction mixture to recover a hydrocarbon solution of the complex carbonated barium phenate sulfide salt.

5. A process for producing a complex carbonated barium phenate sulfide salt which comprises the following sequence of steps: (1) interacting a hydrocarbon solution of a nonyl phenol sulfide, prepared by the reaction of about 4 mol proportions of nonyl phenol with 3 mol proportions of sulfur dichloride, with barium methylate in a proportion to supply to the reaction from at least about 1.2 to about 1.6 equivalents of barium per equivalent of phenol hydroxyl supplied by the phenol sulfide reactant, at a temperature of from about 80° C. to about 150° C., (2) increasing the temperature of the reaction mixture to from about 125° C. to about 200° C., (3) intimately contacting the reaction mixture at said latter temperature with carbon dioxide in sufficient amount and for a sufficient time to incorporate in the complex salt product from at least about 0.2 to at least about 0.6 equivalent of carbon dioxide per equivalent of phenol hydroxyl combined in said product, (4) lowering the temperature of the reaction mixture to from about 80° C. to about 150° C., (5) interacting the reaction mixture at said latter temperature with additional barium alcoholate in an amount to supply to the reaction from about 0.6 to about 1.0 equivalent of barium per equivalent of phenol hydroxyl originally supplied by the alkyl phenol sulfide reactant, (6) again raising the temperature of the reaction mixture to a level of from about 125° C. to about 200° C. and (7) filtering the reaction mixture to recover a hydrocarbon solution of the complex carbonated barium phenate sulfide salt.

6. The process according to claim 5 wherein the reaction mixture from step 6 is subjected to further carbonation and further reaction with metal alcoholate as recited in steps 3 to 6, inclusive, to incorporate additional carbon dioxide and barium in the complex salt.

7. A process for producing a complex carbonated sodium phenate sulfide salt which comprises the following sequence of steps: (1) interacting a hydrocarbon solution of a nonyl phenol sulfide, prepared by the reaction of about 4 mol proportions of nonyl phenol with 3 mol proportions of sulfur dichloride, with sodium methylate in a proportion to supply to the reaction from at least about 1.2 to about 1.6 equivalents of sodium per equivalent of phenol hydroxyl supplied by the phenol sulfide reactant, at a temperature of from about 80° C. to about 150° C., (2) increasing the temperature of the reaction mixture to from about 125° C. to about 200° C., (3) intimately contacting the reaction mixture at said latter temperature with carbon dioxide in sufficient amount and for a sufficient time to incorporate in the complex salt product from at least about 0.2 to at least about 0.6 equivalent of carbon dioxide per equivalent of phenol hydroxyl combined in said product, (4) lowering the temperature of the reaction mixture to from about 80° C. to about 150° C., (5) interacting the reaction mixture at said latter temperature with additional sodium alcoholate in an amount to supply to the reaction from about 0.6 to about 1.0 equivalent of sodium per equivalent of phenol hydroxyl originally supplied by the alkyl phenol sulfide reactant, (6) again raising the temperature of the reaction mixture to a level of from about 125° C. to about 200° C. and (7) filtering the reaction mixture to recover a hydrocarbon solution of the complex carbonated sodium phenate sulfide salt.

8. A process for producing a complex carbonated metal phenate sulfide salt which comprises the following sequence of steps: (1) interacting a hydrocarbon solution of a nonyl phenol sulfide, prepared by the reaction of about 4 mol proportions of nonyl phenol with 3 mol proportions of sulfur dichloride, with magnesium methylate in a proportion to supply to the reaction from at least about 1.2 to about 1.6 equivalents of magnesium per equivalent of phenol hydroxyl supplied by the phenol sulfide reactant, at a temperature of from about 80° C. to about 150° C., (2) increasing the temperature of the reaction mixture to from about 125° C. to about 200° C., (3) intimately contacting the reaction mixture at said latter temperature with carbon dioxide in sufficient amount and for a sufficient time to incorporate in the complex salt product from at least about 0.2 to at least about 0.6 equivalent of carbon dioxide per equivalent of phenol hydroxyl combined in said product, (4) lowering the temperature of the reaction mixture to from about 80° C. to about 150° C., (5) interacting the reaction mixture at said latter temperature with additional magnesium alcoholate in an amount to supply to the reaction from about 0.6 to about 1.0 equivalent of magnesium per equivalent of phenol hydroxyl originally supplied by the alkyl phenol sulfide reactant, (6) again raising the temperature of the reaction mixture to a level of from about 125° C. to about 200° C. and (7) filtering the reaction mixture to recover a hydrocarbon solution of the complex carbonated magnesium phenate sulfide salt.

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# CERTIFICATE OF CORRECTION

Patent No. 2,916,454 December 8, 1959

John S. Bradley V, et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 13, line 13, for "Sodium, percent" read -- Sulfur, percent --.

Signed and sealed this 1st day of November 1960.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents