

[54] **PROCESS FOR PREPARATION OF OVER-BASED SULFURIZED PHENATES**

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[58] Field of Search.....**260/137, 609, 608**

[56] **References Cited**

UNITED STATES PATENTS

3,464,970	9/1969	Sakai et al.	260/137
3,437,595	4/1969	Coupland	260/137 X

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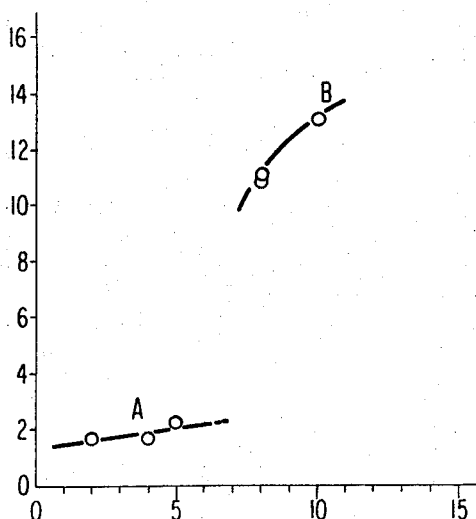
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[57] **ABSTRACT**

A process for the preparation of an over-based sulfurized phenate which comprises the steps of heating a mixture of a phenolic compound, elementary sulfur, an alkaline earth metal reagent such as an oxide of a hydroxide of an alkaline earth metal, and a dihydric alcohol at a temperature of from 110° to 200°C in the presence of a higher alcohol as solvent, wherein the weight ratio of the higher alcohol to the phenolic compound is at least 0.5, preferably at least 3.0, to thereby effect sulfurization and metal addition in parallel, distilling the reaction mixture at a temperature below 200°C to remove water formed in the reactions together with a major portion of any unreacted dihydric alcohol, and heating the reaction product contained in the distillation residue together with carbon dioxide at a temperature of from 70° to 200°C in the presence of the higher alcohol, wherein the weight ratio of the higher alcohol to the phenolic compound is at least 10.5, is disclosed.

27 Claims, 1 Drawing Figure

MINIMUM LAURYL ALCOHOL AMOUNT
REQUIRED TO OBTAIN PHENATES, -
(NUMBER OF GRAMS OF LAURYL ALCOHOL
PER GRAM OF P-OCTYLPHENOL).



BLEND RATIO OF CALCIUM OXIDE TO
P-OCTYLPHENOL, -(EQUIVALENTS OF CALCIUM
OXIDE PER HYDROXYL EQUIVALENT IN
P-OCTYLPHENOL).

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PROCESS FOR PREPARATION OF OVER-BASED SULFURIZED PHENATES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an improvement in the preparation of an oil-soluble over-based sulfurized phenate which is useful as a detergent for lubricating oils as well as a stabilizer for fuel oils. The process of this invention is advantageous over known processes for preparing over-based sulfurized phenates in that more than 700 percent of the theoretical amount of the alkaline earth metal reagent can be reacted with the phenolic compound simultaneously.

2. Description of the Prior Art

Recently, low-grade fuel oils with high sulfur content have come to be used widely in diesel engines, particularly in large marine diesel engines. In order to eliminate the detrimental effects of acids formed by the use of such fuel oils, alkaline detergent additives, especially the so-called phenates or sulfurized phenates, capable of neutralizing the acids have been used widely in lubricants use to lubricate these engines. Of these phenates, those containing an alkaline earth metal in the theoretical amount per hydroxyl radical of the phenolic compound, i.e., those containing an alkaline earth metal in a proportion of $\frac{1}{2}$ atom per hydroxyl radical of the phenolic compound, are generally called normal phenates and have been used for years. As the grade of fuel oils decreases, however, basic phenates containing more than the theoretical amount of alkaline earth metal, the so-called over-based phenates having a higher alkaline earth metal content than the basic phenates, have been requires. These phenates are also used to stabilize fuel oils.

Two processes for the preparation of the over-based sulfurized phenates are known; in one process a phenolic compound is first sulfurized with a sulfurizing agent, such as sulfur monochloride, to obtain a sulfide, which is then reacted with an alkaline earth metal reagent; in the second process a phenolic compound, elementary sulfur, an alkaline earth metal reagent and a dihydric alcohol are heated to effect the sulfurization and the metal addition in parallel or simultaneously. It has been reported that these two processes result in products having different structures and properties. The present invention relates to the latter of these two processes.

United States Pat. No. 3,464,970 and Japanese Pat. No. 533,079, filed in the names of the same inventors as the present invention, disclosed a process for the production of over-based sulfurized phenates comprising the steps of heating a mixture of a phenolic compound, elementary sulfur, a dihydric alcohol and an oxide or hydroxide of alkaline earth metal at a temperature of from 110° to 200°C in a higher alcohol solvent in the amount of from 0.5 to 10.0 times the weight of the phenolic compound thereby to effect sulfurization and metal addition in parallel, removing the water formed and a major portion of unreacted dihydric alcohol by distillation from the reaction mixture at a temperature below 200°C, then subjecting the resulting residue to a treatment with carbon dioxide. In these processes, however, it is clear that the maximum amount of the alkaline earth metal compound which can be reacted smoothly at one time with the phenolic

compound is limited, for example, up to about 600 percent of the theoretical value, and the addition of a further excess of the alkaline earth metal compound with the intention of reacting considerably more alkaline earth metal compound at once often results in the solidification of the reaction product upon treatment with carbon dioxide or other operations rendering subsequent operations impossible. In these prior processes, for example, wherein p-octylphenol is used as the phenolic compound, the metal addition reaction and the carbon dioxide treatment must be conducted repeatedly at least twice in order to obtain smoothly an oil-soluble overbased sulfurized phenate using an alkaline earth metal compound in the amount of 700 percent of the theoretical value, i.e., by using seven equivalents of the alkaline earth metal compound per equivalent of hydroxyl radical in the phenolic compound.

Process similar to those described in U.S. Pat. No. 3,464,970 and Japanese Pat. No. 533,079 are also disclosed in U.S. Pat. Nos. 2,680,096 and 3,036,971 and British Pat. No. 900,059. In these processes, however, the use of a higher alcohol is not contemplated, and the amount of an alkaline earth metal compound which can be reacted with a phenolic compound at one time is not more than about 170 percent or 200 percent of the theoretical. Additionally, the yield of the phenate obtained is poor based on the alkaline earth metal reagent used in the reaction.

Moreover, U.S. Pat. No. 3,178,368 discloses a process whereby the alkaline earth metal compound is reacted in an amount as high as up to 450 percent of the theoretical. This method, however, requires the combined use of an alkylaryl sulfonate, as the starting material, and the alkaline earth metal content of 450 percent of the theoretical is derived from the sulfonate as well.

One of the primary objects of the present invention is to provide an improved process wherein more than 700 percent of the theoretical amount of the alkaline earth metal reagent can be reacted with a phenolic compound at one time to obtain an over-based sulfurized phenate.

Another object of the invention is to provide a process for preparing an over-based sulfurized phenate with high alkaline earth metal content not requiring the use of an alkylaryl sulfonate.

These and other objects of the present invention will become apparent from the ensuing description and the appended claims.

SUMMARY OF THE INVENTION

The invention provides an improvement in a process for the preparation of over-based sulfurized phenates. The process of this invention comprises the steps of reacting a phenolic compound, elementary sulfur, an alkaline earth metal compound and a dihydric alcohol to effect sulfurization and metal addition in parallel or simultaneously, removing the water formed and a major portion of the unreacted dihydric alcohol from the reaction product, and subjecting the resultant reaction product to a carbon dioxide treatment. The invention also provides a process whereby at least 700 percent of the theoretical amount of an alkaline earth metal compound can be reacted with the phenolic compound at one time.

BRIEF DESCRIPTION OF THE INVENTION

More particularly, the process of this invention comprises heating at a temperature of from 110° to 200°C a mixture of (a) at least one phenolic compound selected from the group consisting of phenol and alkylphenols, (b) elementary sulfur, (c) an alkaline earth metal reagent selected from the group consisting of an alkaline earth metal oxide and an alkaline earth metal hydroxide in the amount at least seven equivalents of the alkaline earth metal per equivalent of hydroxyl radical of said phenolic compound, and (d) a dihydric alcohol, in the presence of a higher alcohol having a boiling point higher than that of the dihydric alcohol used, said higher alcohol containing from 9 to 24 carbon atoms, and wherein the weight ratio of the higher alcohol to the phenolic compound is at least 0.5, preferably at least 3.0, to thereby effect sulfurization and metal addition in parallel, distilling the reaction mixture at a temperature below 200°C to remove substantially all of the water formed in the reactions and a major portion of the unreacted dihydric alcohol, then heating the reaction product contained in the residue from the distillation at a temperature of from 70° to 200°C together with carbon dioxide in the presence of the higher alcohol, wherein the ratio by weight of the higher alcohol to the phenolic compound is at least 10.5, to obtain an over-based sulfurized phenate having an alkaline earth metal content of more than 700 percent based on the theoretical amount.

The invention also is intended to cover a process involving subjecting the carbon dioxide-treated mixture obtained above to further metal addition by adding the alkaline earth metal reagent and the dihydric alcohol repeatedly, distilling off the water formed and the unreacted dihydric alcohol, and subjecting the distillation residue resulting to additional carbon dioxide treatment to obtain higher over-based sulfurized phenates.

BRIEF DESCRIPTION OF THE DRAWING

The present invention can be easily understood by reference to the graph shown in the attached drawing. The graph illustrates the results obtained in the process of this invention in comparison with results obtained in the process described in U.S. Pat. No. 3,464,970, including the minimum requisite amounts of the higher alcohol required to obtain the oil-soluble over-based sulfurized phenates containing varying amounts of alkaline earth metal. These experiments were carried out using p-octylphenol, as the phenolic compound, commercially available lauryl alcohol, as the higher alcohol, calcium oxide as the alkaline earth metal reagent and ethylene glycol as the dihydric alcohol. In the graph, the abscissa indicates the blending ratio of the calcium oxide to the p-octylphenol, i.e., the number of equivalents of calcium used per equivalent of the hydroxyl radical of the p-octylphenol used. The ordinate indicates the minimum or slightly excess amount of lauryl alcohol required to obtain the respective phenates, i.e., the number of grams of lauryl alcohol used per gram of p-octylphenol reacted.

Curve A shows the results obtained in Comparative Examples 4, 6 and 7, which are set forth hereinafter in the specification, carried out in accordance with the process described in U.S. Pat. No. 3,464,970.

Curve B shows the results obtained in Example 1-3, which are described hereinafter in the specification, carried out in accordance with the process of this invention.

The results show a marked increase from Curve A to Curve B at from six to seven equivalents in the amount of the calcium oxide used per equivalent amount of the hydroxyl radical in the p-octylphenol used.

DETAILED DESCRIPTION OF THE INVENTION

As described hereinbefore, this invention relates to a process for preparing an over-based sulfurized phenate having a high alkaline earth metal content.

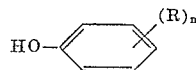
It has been found that in accordance with the present invention, it is possible to produce an oil-soluble over-based phenate containing more than 700 percent to the theoretical of an alkaline earth metal by heating at a temperature of from 110° to 200°C a mixture of a phenolic compound, elementary sulfur, an alkaline earth metal reagent and a dihydric alcohol in the presence of a higher alcohol, wherein the weight ratio of the higher alcohol to the phenolic compound used is at least 0.5, preferably at least 3.0, to thereby effect sulfurization and metal addition in parallel, distilling the reaction mixture at a temperature below 200°C to remove the water formed and a major portion of the untreated dihydric alcohol, then heating the reaction product contained in the distillation residue at a temperature of from 70° to 200°C together with carbon dioxide in the presence of the higher alcohol, wherein the weight ratio of the higher alcohol to the phenolic compound used in the reaction is at least 10.5.

According to the process of this invention, the alkaline earth metal compound can be reacted with the phenolic compound in the amount of 700 percent or more to the theoretical value.

In the process described in U.S. Pat. No. 3,464,970 and Japanese Pat. No. 533,079 where phenolic compounds, elementary sulfur, alkaline earth metal reagents and dihydric alcohols are used as the starting materials and higher alcohols are used as the solvent, the amount of the alkaline earth metal reagents to be reacted at one time reaches a maximum at about 500 percent of the theoretical and it has been thought that an upper limit in which liquid products could be obtained existed.

Nevertheless, it has been found unexpectedly that the amount of alkaline earth metal reagent to be reacted at one time with the phenolic compound can be increased as high as 700 percent or more to the theoretical value by the improved operations of this invention involving the use of much larger quantity of higher alcohol used as the solvent than that employed in the process described in the above patents. The use of the higher alcohol, wherein the ratio by weight of the higher alcohol to the phenolic compound used is at least 10.5, in the carbon dioxide treatment, preferably in the entire process, thereby enables the production of an over-based sulfurized phenate containing an extremely large amount of an alkaline earth metal.

The phenolic compounds employed in the present invention are those represented by the following general formula



wherein R is an alkyl group containing at least one, preferably from 1 to 50 carbon atoms, and n is an integer of from 0 to 3.

Typical phenolic compounds include, for example, phenol, butylphenol, amylphenol, octylphenol, dioctylphenol, nonylphenol, dinonylphenol, dodecylphenol, cetylphenol, higher alkylphenols having groups derived from various olefine polymers such as polypropylene, polybutylene, and the like, and mixtures thereof. The group derived from the olefin polymers usually contains from 9 to 125 carbon atoms. In some instances, however, a higher molecular weight group, for example, one containing from about 3500 to 7000 carbon atoms (giving rise to a molecular weight of from about 50,000 to 100,000) can be used as well since it has been found that such a group can impart viscosity index improving properties to the phenate.

As the alkaline earth metal reagent, oxides or hydroxides of alkaline earth metals are preferred. Though the alkaline earth metal reagent includes, for example, oxides or hydroxides of barium or magnesium, calcium oxide or calcium hydroxide is preferred.

The alkaline earth metal reagent can be added in any desired amount of at least seven equivalents per equivalent of hydroxyl radical of the phenolic compound. In this process, the rate of the reaction of the alkaline earth metal reagent is usually high, so it will not be necessary to use it in large excess to that desired in the reaction product.

The dihydric alcohol to be used is preferably one having a relatively low boiling point, low viscosity and high reactivity. Typically, such dihydric alcohols are those having from 2 to 6 atoms. Ethylene glycol is most preferred. The amount of dihydric alcohol used varies depending upon the amounts of the alkaline earth metal reagent and elementary sulfur used, but should be at least 0.5 mol per mol of the alkaline earth metal reagent. However, the dihydric alcohol acts per se as a solvent and, hence, is usually used in excess.

Elementary sulfur is used in the amount of from 0.5 to 4.5 g atoms, preferably 1.0–3.5 g atoms, per mol of the phenolic compound, although the amount can vary slightly depending upon the amount of the alkaline earth metal reagent, the type of phenolic compound and the reaction condition used.

The higher alcohol used as the solvent is a straight chain or branched aliphatic saturated monohydric alcohol having at least 9 carbon atoms and is one having a boiling point higher than that of the dihydric alcohol used.

The higher alcohol desirably has less than 24 carbon atoms. From 9 to 24 carbon atoms is preferred, and from 9 to 18 carbon atoms is especially preferred, because the recovery of the higher alcohol from the carbon dioxide-treated mixture is much easier where the number of carbon atoms is below 24. The higher alcohol should be used as the solvent in the sulfurization and metal addition reactions in an amount of at least 0.5, preferably at least 3.0, times the weight of the phenolic compound used. The higher alcohols must be used as the solvent in the subsequent carbon dioxide treatment, in an amount of at least 10.5 times the weight of the phenolic compound used. In the practice of the process of this invention, it is necessary to use the higher alcohol solvent in an amount as much as

10.5 times or higher to the weight of the phenolic compound used in the carbon dioxide treatment to attain the reaction of the alkaline earth metal reagent in any desired amount in excess of 700 percent of the theoretical value at one time with the phenolic compound. Of course, the higher alcohol in the amount of as much as 10.5 or more times the weight of the phenolic compound used can be used in any previous step, i.e., in the removal of the water and dihydric alcohol, or in the sulfurization and metal addition reactions and the removal of water and dihydric alcohol. Use of lesser amounts of the higher alcohol than the above-mentioned amount will result in difficulty in the reaction progressing and in the handling of the reaction product due to the solidification, especially upon the carbon dioxide-treatment, to such an extent that subsequent operations become no longer possible. The larger the amount of the higher alcohol solvent used, the larger the amount of the alkaline earth metal reagent to be reacted at one time with the phenolic compound. The use of the higher alcohol solvent insures easy handling of the reaction product, easy removal of the water and the dihydric alcohol and also facilitates the carbon dioxide treatment.

The detailed mechanism of how the higher alcohol enables the production of the over-based sulfurized phenates containing a large amount of alkaline earth metal is not yet understood. The higher alcohol can be used in the amount several hundred times the weight of the phenolic compound used, especially after the sulfurization and metal addition. However, it is disadvantageous to use too excessive an amount of the higher alcohol from an economical point of view. The minimum requisite amount of the higher alcohol varies slightly with each phenolic compound.

In the present invention, a lubricating oil can be added, similar to the known art, as a diluent either prior to, during the course of, or after the reactions so as to facilitate the handling of the reaction product. Such lubricating oils preferably include synthetic lubricants and petroleum lubricants, such as naphthenic base, paraffinic base and mixed base lubricating oils.

In the present invention, the sulfurization and the metal addition are carried out in parallel or simultaneously. That is, the sulfurization and metal addition reactions are carried out by mixing the phenolic compound, elementary sulfur, the alkaline earth metal reagent and the dihydric alcohol with the higher alcohol in which the weight ratio of the higher alcohol to the phenolic compound used is at least 0.5, preferably at least 3.0, then heating the resultant mixture at a temperature of 110° to 200°C. Although an accurate mechanism for these reactions is not yet understood, it has been experimentally determined that the metal addition takes place at a temperature of from about 20° to 200°C, and the sulfurization substantially takes place when the metal addition reaction starts, at least partially, and when the temperature of the mixture is from 110° to 200°C. There is no particular order of the addition of each material, especially of the elementary sulfur, the alkaline earth metal reagent and the dihydric alcohol. They can be added separately. When the sulfurization does not proceed satisfactorily, it is necessary to heat the mixture at a temperature about 110°C in

order to complete substantially the sulfurization and the metal addition, and it is also necessary to stir the mixture at a temperature above 20°C when the metal addition does not take place sufficiently.

It is of course convenient to carry out both the sulfurization and the metal addition reaction essentially at the same time, so that the entire reagents are usually heated, in combination, at a temperature of from 110° to 200°C. However, it is preferred that the reaction temperature for sulfurization and metal addition be maintained within the range of from 110° to 200°C, desirably from 120° to 190°C, since an excessively high temperature can cause undesirable side reactions and since at lower temperatures than the above range the reaction takes place with difficulty. In view of commercial productivity or yield, the sulfurization and metal addition reactions are most preferably carried out by maintaining the temperature within the range of from 110° to 150°C. The hydrogen sulfide generated during the reaction is removed out of the system. The time for substantial completion of the sulfurization varies depending on the reaction temperature, the amount of the reactants used and the manner of stirring. The course of the reaction can be followed or determined by measuring the amount of hydrogen sulfide generated, with the sulfurization being completed substantially when the amount of hydrogen sulfide generated is less than one half, preferably less than one fourth of that of the maximum generation.

The sulfurization and metal addition reactions can be conducted under reduced pressure while distilling of the water formed in the reaction and dihydric alcohol. In this case, however, the amount of dihydric alcohol should be controlled in such a manner that at least the minimum required amount of the dihydric alcohol is kept in the reaction mixture until the sulfurization and metal addition process sufficiently. The sulfurization and metal addition are completed within from 1 to 10 hours. If removal of water formed is insufficient and an excess of dihydric alcohol remains in a large amount, a large amount of insolubles forms in the carbon dioxide treatment to lower the product yield, so that substantially all of the water formed in the reactions and a major portion of unreacted dihydric alcohol must be removed during the reactions or after the reactions by subjecting the reaction mixture to distillation under reduced pressure at a temperature below 200°C. This step is usually carried out under such conditions that a major portion of the higher alcohol used is not distilled off to keep the residue in solution.

The distillation residue freed from the water and a major portion of the unreacted dihydric alcohol is then brought into contact with carbon dioxide. This carbon dioxide treatment is carried out by heating the reaction product contained in the distillation residue together with carbon dioxide in the presence of a large amount of the higher alcohol, as much as at least 10.5 times the weight of the phenolic compound used for the reactions.

Where the previous sulfurization and metal addition reactions are carried out in the presence of the higher alcohol in which the weight ratio of the higher alcohol to the phenolic compound used is from about 0.5 to about 10.5, supplementary higher alcohol is added before the carbon dioxide treatment, preferably prior to

the removal of water and dihydric alcohol, in an amount of the higher alcohol such that the product mixture contains a total of at least 10.5 times the weight of the phenolic compound used in the reactions. The carbon dioxide treatment is preferably carried out at normal or elevated pressure at a temperature of from 70° to 200°C. After the absorption of carbon dioxide has been completed, the reaction product (treated with carbon dioxide) is preferably maintained under the atmosphere of gas comprising primarily carbon dioxide at a temperature of from 120° to 200°C for a period of from several minutes to ten or more hours in order to assure completion of the reaction. By this treatment, the product is also improved in its stability against water and heat as well as in oil-solubility.

Where the above sulfurization and metal addition reactions are carried out at from 110° to 150°C, subsequent procedures, such as the additional metal addition reaction, the removal of water and the dihydric alcohol, and the carbon dioxide absorption, are conducted preferably at a temperature below 150°C to prevent side reactions. When the sulfurization and metal addition reactions are carried out at from 155° to 220°C, the subsequent procedures are desirably conducted at a temperature below 200°C.

The carbon dioxide-treated product mixture can be further reacted with at least one equivalent of the alkaline earth metal reagent per equivalent of the hydroxyl radical in the phenolic compound used and at least 0.5 mol of the dihydric alcohol per mol of the alkaline earth metal reagent can be added to effect additional metal addition at from 20° to 200°C. Then, the reaction mixture is distilled to remove substantially all the water and a major portion of the unreacted dihydric alcohol at a temperature below 200°C, and the distillation residue is treated again with carbon dioxide at from 70° to 200°C with at least one more repetition to reaction additional alkaline earth metal reagent.

Since the product mixture obtained after the carbon dioxide treatment contains the higher alcohol, economically it is desirable to recover a major portion of or the entire amount of the higher alcohol. The removal of the higher alcohol is preferably effected by distilling the resulting mixture, preferably after the carbon dioxide treated mixture has been incorporated with a lubricating oil. In the process of this invention, insolubles due to unreacted materials and by-products due to side reactions are formed in extremely minor amounts. These insolubles are removed, either before or after the recovery of the higher alcohol, by means of filtration, centrifugal separation or the like operations.

Thus, in accordance with the present invention, an oil-soluble over-based sulfurized phenate having an extremely high alkaline earth metal content can be obtained advantageously at a good yield. The alkaline earth metal reagent can be reacted at one time in an amount as much as 700 percent or more of the theoretical value. The over-based sulfurized phenates so obtained are used not only as detergents for lubricating oils but also as stabilizers for fuel oils.

The scope of this invention is not intended to be limited by any theory, but Curve B in the graph shown in the drawing is a plot of the results obtained in Examples 1-3 of this invention, and cannot be obtained by an extrapolation of Curve A which is a plot of the results

obtained in Comparative Examples 4, 6 and 7 performed according to the process described in U.S. Pat. No. 3,464,970. It is thought that such a marked increase from Curve A to Curve B demonstrates a profound difference in the structure of the over-based sulfurized phenate obtained by reacting more than 700 percent of the theoretical of the alkaline earth metal reagent according to the process of this invention, and the structure of a known over-based sulfurized phenate obtained by reacting up to 600 percent of the theoretical of the alkaline earth metal reagent according to the above described prior process.

The present invention will be illustrated by reference to the following examples.

EXAMPLE 1

To a suspension containing 103.2 g (0.5 mol) of p-octylphenol, 114.4 g (4.0 g equivalents) of calcium oxide (purity 98 percent by weight), 1135.2 g (11.0 times the weight of the p-octylphenol used) of lauryl alcohol and 22.5 g (0.7 g atom) of elementary sulfur, there was added 298.1 g (4.8 mols) of ethylene glycol at 135°C and the mixture was stirred at the same temperature for 5 hours, while removing the hydrogen sulfide generated, to give 1664 g of solution. From 1414 g of this solution, water and a major portion of ethylene glycol were distilled off under reduced pressure to give 1113 g of a residue. The final distillation temperature was 123°C at 14 mmHg.

Into 270.6 g of the distillation residue, carbon dioxide was introduced at 125° to 132°C under pressure (up to 11 kg/cm²) to effect absorption, and the mixture was kept at 145°C for an additional one hour to give 276.6g of a carbon dioxide-treated mixture. To 275.1 g of the resultant mixture, 100.0 g of lubricating oil (viscosity of 3.34 cs at 210°F) was added, and the resultant mixture was distilled under reduced pressure to remove a small amount of the ethylene glycol, a major portion of the lauryl alcohol, and a small portion of the lubricating oil to give 151.5 g of a residual material. The final distillation temperature under 5 mmHg was 167°C. After removing the insolubles by filtration from the above residue, there was obtained 142.5 g of a dark yellowish red transparent liquid product having the following characteristics:

Viscosity, 210°F (cs)	84.06
Total Base Number (JIS K-2502*)	254
Calcium Content (wt. %)	9.23
Carbon Dioxide Content (wt. %)	7.81
Sulfur Content (wt. %)	2.57

* Japanese Industrial Standards K-2502 "Testing Method for Neutralization Value of Petroleum Product."

EXAMPLE 2

To a suspension containing 82.6 g (0.4 mol) of p-octylphenol, 115.0 g (4.0 g equivalents) of calcium oxide (purity 98 percent by weight) 826.0 g (10.0 times the weight of the p-octylphenol used) of lauryl alcohol and 18.0 g (0.56 g atom) of elementary sulfur, there was added 249.0 g (4.0 mols) of ethylene glycol at 136°C and the mixture was stirred at the same temperature for 5 hours, with the removal of hydrogen sulfide generated, to give thereby 1284.8 g of a solution.

From 1278.6 g of this solution, water and a major portion of the ethylene glycol were distilled off in a nitrogen stream under reduced pressure to give 1072.9 g of a residue. The final distillation temperature was 124°C at 20 mmHg.

To 249.0 g of this residue was admixed 57.7 g (equivalent to 3.0 times the weight of the p-octylphenol used) of lauryl alcohol, and carbon dioxide was introduced to the resultant mixture at 114°-124°C under a pressure (up to 10 kg/cm²) to effect absorption. Then the mixture was kept at 160°C for an additional 2 hours to give 316.9 g of a carbon dioxide-treated mixture. To 302.2 g of the resultant mixture was added 106.0 g of a lubricating oil (viscosity of 3.34 cs at 210°C) and the mixture was distilled under a reduced pressure to remove a small amount of the ethylene glycol together with a major portion of the lauryl alcohol and a minor portion of the lubricating oil to give 164.9 g of a residue. The final distillation temperature was 170°C at 6 mmHg. After the removal of the insolubles from the residue, 159.2 g of a dark, yellowish red transparent liquid product having the following characteristics were obtained.

Viscosity, 210°F (cs)	23.06
Total Base Number (JIS K-2502)	253
Calcium Content (wt. %)	9.24
Carbon Dioxide Content (wt. %)	8.22
Sulfur Content (wt. %)	2.29

EXAMPLE 3

To a suspension containing 113.5 g (0.55 mol) of p-octylphenol 125.8 g (4.4 g equivalents) of calcium oxide (purity 98 percent by weight) 1248.5 g (11.0 times the weight of the p-octylphenol used) of lauryl alcohol and 24.7 g (10.77 g atom) of elementary sulfur, there was added at 165°C 331.2 g (5.3 mols) of ethylene glycol and the mixture was stirred at the same temperature for 6 hours, with the removal of hydrogen sulfide, to give 1829 g of a solution. From 1784 g of the solution, water and a major portion of the unreacted ethylene glycol were distilled off under reduced pressure to give 1458 g of a residue. The final distillation temperature was 141°C.

To 265.8 g of the residue, carbon dioxide was introduced under a pressure (up to 11 kg/cm²) at 120°-131°C to effect the absorption, and the mixture was kept at 170°C for an additional one hour to give 273.5 g of a carbon dioxide-treated mixture. To 271.7 g of the mixture was added 100.0 g of a lubricating oil (viscosity of 3.34 cs. at 210°F), and the resultant mixture was distilled under a reduced pressure to remove a small amount of the ethylene glycol together with a major portion of the lauryl alcohol and a small portion of the lubricating oil to give 148.2 g of a residue, from which the insolubles were removed to give 137.4 g of a liquid product having the following characteristics:

Viscosity, 210°F (cs)	75.02
Total Base Number (JIS K-2502)	252
Calcium Content (wt. %)	9.22
Carbon Dioxide Content (wt. %)	8.05
Sulfur Content (wt. %)	2.50

COMPARATIVE EXAMPLE 1

To a suspension containing 123.8 g (0.6 mol) of p-octylphenol, 137.3 g (4.8 g equivalents) of calcium oxide (purity 98 percent by weight), 991.0 g (8.0 times the weight of the p-octylphenol used) of lauryl alcohol and 27.0 g (0.84 g atom) of elementary sulfur, there was added 253.5 g (4.1 mols) of ethylene glycol at 135°C and the mixture was stirred at the same temperature for 4 hours, with the removal of hydrogen sulfide. Removal by distillation of the water and a major portion of the ethylene glycol under a nitrogen stream under a reduced pressure gave 1252 g of a residue. The final distillation temperature was 123°C at 12 mmHg.

Carbon dioxide was introduced into 454.1 g of the residue at 123°–138°C under a pressure (up to 11 kg/cm²) so as to effect absorption. However, the subsequent operations became impossible due to an abrupt solidification of the reaction product during the carbon dioxide treatment.

COMPARATIVE EXAMPLE 2

To 249.6 g of the residue obtained in Comparative Example 1 was added 24.5 g (equivalent equally to the weight of p-octylphenol used) of lauryl alcohol. Introduction to this mixture of carbon dioxide at 122°–158°C under a pressure to effect absorption resulted in the formation of a solid mass and no further operation was possible

COMPARATIVE EXAMPLE 3

The procedure of the sulfurization and metal addition operation of Example 3 was repeated except that 908.0 g (8.0 times the weight of the p-octylphenol used) of lauryl alcohol was used. The removal of water and a major portion of the unreacted ethylene glycol gave 1082 g of a residue, to which carbon dioxide was introduced at 122°–134°C under a pressure. However, further operation was impossible due to the solidification of the reaction product.

The following Comparative Examples 4–7 were carried out to determine the minimum required amount of higher alcohol needed to obtain an over-based sulfurized phenate according to the process described in U.S. Pat. No. 3,464,970.

COMPARATIVE EXAMPLE 4

To a mixture comprising 82.6 g (0.4 mol) of p-octylphenol, 45.7 g (1.6 g equivalents) of calcium oxide (purity 98% by weight), 16.2 g (0.51 g atom) of elementary sulfur, 134.6 g (1.63 times the weight of the p-octylphenol used) of lauryl alcohol and 165.4 g (2.0 times the weight of the p-octylphenol used) of a lubricating oil (viscosity of 3.34 cs at 210°F), there was added dropwise 84.6 g (1.36 mols) of ethylene glycol at 135°C and the resultant mixture was stirred at the same temperature for 5 hours, with the removal of hydrogen sulfide, to give mixture in a yield of 521.1 g. After removing water and a major portion of the ethylene glycol under a reduced pressure, from 510.7 g of this mixture 405.5 g of a distillation residue was obtained. The final distillation temperature was 120°C at 7 mmHg. There was observed the formation of a small amount of a gellike solid in this residue.

Carbon dioxide was then introduced into 388.0 g of the residue at 130°C under a pressure (up to 10

Kg/cm²), and the residue was kept at 160°C for an hour to complete the absorption to give 407.6 g of the carbon dioxide treated mixture. From 403.5 g of this mixture were removed by distillation under a reduced pressure a small amount of the ethylene glycol, a major portion of the lauryl alcohol and a small portion of the lubricating oil to give as the residue 277.7 g of the product mixture. The final distillation temperature was 193°C at 9 mmHg. The removal of 6.5 g of insolubles from this product mixture gave 271.1 g of a dark red viscous liquid product with a viscosity of 211.7 cs (217°F) and total base number of 274.

COMPARATIVE EXAMPLE 5

The procedure of Comparative Example 4 was repeated except that the amount of calcium oxide used was 2 equivalents per equivalent of that hydroxyl radical of the p-octylphenol used, the lauryl alcohol used was 0.8 times the weight of the p-octylphenol used, and addition of the lubricating oil to the system was carried out before the removal of the lauryl alcohol, so as to prepare an over-based sulfurized phenate. There was observed a large amount of gel formation in the residue upon the removal of water and ethylene glycol, and the subsequent operations were carried out with difficulty leading to a poor yield of phenate.

COMPARATIVE EXAMPLE 6

The procedure of Comparative Example 4 was repeated except that the amount of calcium oxide used was two equivalents per equivalent of the hydroxyl radical of the p-octylphenol used, the lauryl alcohol used was 1.62 times the weight of the p-octylphenol used, the lubricating oil was added before the removal of the lauryl alcohol and the lubricating oil used was 1.2 times the weight of the p-octylphenol used, so as to prepare an over-based sulfurized phenate. There was observed a small amount of gel formation in the residue during the removal of water and ethylene glycol. The final liquid product thus obtained has a viscosity of 178 cs (210°F) total a total base number of 209.

COMPARATIVE EXAMPLE 7

The procedure of Comparative Example 4 was repeated except that the calcium oxide used was five equivalents per equivalent of the hydroxyl radical of the p-octylphenol and the lauryl alcohol used was 2.2 times the weight of the p-octylphenol used and the addition of the lubricating oil was conducted before the removal of the lauryl alcohol, so as to prepare an over-based sulfurized phenate. There was observed the formation in a small amount of a gel-like solid in the residue upon the removal of water and the ethylene glycol. The final liquid product thus obtained has a viscosity of 307.9 cs (210°F) and a total base number of 284.

The results obtained in Examples 1, 2 and 3, wherein calcium oxide was reacted in an amount of 800 percent, 1000 percent and 800 percent of the theoretical value using lauryl alcohol in an amount of 11.0, 13.0 and 11.0 times the weight of the p-octylphenol used, respectively, to give oil-soluble products, were plotted as Curve B in the graph in the drawing. The results obtained in Comparative Examples 1 to 3 are shown to

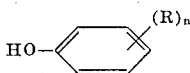
explain the fact that oil-soluble products can never be obtained by the reaction at one time of 800 percent of the theoretical of calcium oxide when using lauryl alcohol in the amount of from 8.0 to 9.0 times the weight of the p-octylphenol used.

Comparative Examples 4-7 show the preparation of oil-soluble over-based phenates according to the process described in U.S. Pat. No. 3,464,970 wherein 200 to 500 percent of the theoretical amount of calcium oxide was reacted with p-octylphenol. In comparative Examples 4 to 7, the amount of lauryl alcohol used was regarded as its minimum required amount when the product could be obtained in somewhat satisfactory yield, although the formation of some gel-like solid mass was observed during the distilling off of the water and the ethylene glycol to such an extent that no considerable difficulties resulted. Accordingly, the results obtained in Comparative Examples 4, 6 and 7 were plotted as Curve A in the graph.

The graph of the attached drawing with a plot of the results obtained in Comparative Examples 4, 6 and 7 (Curve A), and a plot of the results obtained in Examples 1 to 3 (Curve B) illustrates the relationship between the calcium content to the theoretical in the phenates obtained, that is, the number of equivalents of calcium oxide used per equivalent of hydroxyl radical of the p-octylphenol used, and the minimum required amount of lauryl alcohol to obtain those phenates, i.e., the number of grams of lauryl alcohol used per gram of p-octylphenol used. According to this graph, it can be seen that lauryl alcohol in an amount of at least about 10.5 times the weight of the p-octylphenol used is required in order to obtain an over-based sulfurized phenate having more than about 700 percent by weight of calcium content to the theoretical. It also can be seen that Curve B, showing the results of the present invention, can never be obtained by the extrapolation of Curve A, showing the results of the process of the prior art.

What is claimed is:

1. In a process for preparing an over-based sulfurized phenate by reacting phenolic compound, elementary sulfur, an alkaline earth metal compound and a dihydric alcohol to effect sulfurization and metal addition reactions in parallel, removing water formed and unreacted dihydric alcohol from the reaction product and then subjecting the reaction product to a carbon dioxide treatment, the improvement which comprises mixing at least one phenolic compound having the general formula



wherein R is an alkyl group containing at least one carbon atom, and n is an integer of from 0 to 3 elementary sulfur at a level of from 0.5 to 4.5 g atoms per mol of said phenolic compound, at least seven equivalents of an alkaline earth metal reagent selected from the group consisting of the oxides and the hydroxides of an alkaline earth metal per equivalent of the hydroxyl radical of said phenolic compound, and at least 0.5 mold of a dihydric alcohol having 2-6 carbon atoms per mol of said alkaline earth metal reagent, heating the resultant

mixture at a temperature of from 110° to 200°C in the presence of a higher alcohol having nine to 24 carbon atoms and a boiling point higher than that of said dihydric alcohol, wherein the weight ratio of said higher alcohol to said phenolic compound is at least 0.5, removing substantially all of the water formed in the reaction and a major portion of the unreacted dihydric alcohol by distilling the reaction mixture at a temperature below 200°C, then subjecting the distillation residue containing the reaction product to heating at a temperature of from 70° to 200°C together with carbon dioxide in the presence of said higher alcohol wherein the weight ratio of said higher alcohol to the phenolic compound used is at least 10.5.

2. The process of claim 1, wherein the alkaline earth metal is calcium.

3. The process of claim 1, wherein the dihydric alcohol is ethylene glycol.

4. The process of claim 1, wherein the sulfurization and metal addition reactions are carried out in the presence of a higher alcohol having from 9 to 24 carbon atoms, wherein the weight ratio of said higher alcohol to the phenolic compound used is from 0.5 to 10.5, and the reaction mixture is combined before removal of water and dihydric alcohol, with said higher alcohol in an amount such that the total amount of the higher alcohol in the product mixture is at least 10.5 times the weight of said phenolic compound used.

5. The process of claim 1, wherein the sulfurization and metal addition reactions are carried out in the presence of a higher alcohol having from 9 to 24 carbon atoms, wherein the weight ratio of said higher alcohol to the phenolic compound used is from 0.5 to 10.5, and the distillation residue is combined, before the carbon dioxide treatment, with said higher alcohol in an amount such that the total amount of said higher alcohol in the product mixture is at least 10.5 times the weight of said phenolic compound used.

6. The process of claim 1, wherein the sulfurization and metal addition reactions are carried out in the presence of a higher alcohol having from 9 to 24 carbon atoms, wherein the weight ratio of said higher alcohol to the phenolic compound is at least 10.5.

7. The process of claim 1, wherein the sulfurization and metal addition reactions are carried out in the presence of a lubricating oil as a diluent.

8. The process of claim 1, wherein a lubricating oil is added to the reaction mixture before removing the water and dihydric alcohol.

9. The process of claim 1, wherein the sulfurization and metal addition reactions are carried out under reduced pressure while removing the water formed and dihydric alcohol by distilling.

10. The process of claim 1, wherein a portion of the alkaline earth metal reagent used is added at the beginning of the sulfurization and metal addition reactions, and the remainder of the alkaline earth metal reagent is added after completion of the sulfurization reaction.

11. The process of claim 1, wherein a portion of the dihydric alcohol to be used for the reactions is added at the beginning of the sulfurization and metal addition reactions and the remainder of the dihydric alcohol is added after completion of the sulfurization reaction.

12. The process of claim 1, wherein a portion of the alkaline earth metal reagent and a portion of the dihydric alcohol are added at the beginning of the sulfurization and metal addition reactions, and the remainder of the alkaline earth metal reagent and the remainder of the dihydric alcohol are added after completion of the sulfurization reaction.

13. The process of claim 1, wherein the sulfurization and metal addition reactions are carried out at from 110° to 150°C, the removal of water and dihydric alcohol is carried out by distillation at a temperature below 150°C and the carbon dioxide treatment is first carried out at from 70° to 150°C and then at from 120° to 200°C.

14. The process of claim 1, wherein the sulfurization and metal addition reactions are carried out at from 155° to 200°C.

15. A process for preparing an over-based sulfurized phenate according to claim 1, which further comprises, after the carbon dioxide treatment removing any precipitate and a portion of the higher alcohol from the carbon dioxide-treated mixture.

16. A process for preparing an over-based sulfurized phenate according to claim 1, which further comprises adding a lubricating oil, after the carbon dioxide treatment, to the carbon dioxide-treated mixture, and removing any precipitate and at least a portion of the higher alcohol from said mixture.

17. A process for the preparation of an over-based sulfurized phenate according to claim 1, which further comprises adding to the carbon dioxide-treated mixture, after the carbon dioxide treatment, an alkaline earth metal reagent selected from the group consisting of an oxide or a hydroxide of an alkaline earth metal and a dihydric alcohol having from 2 to 6 carbon atoms, heating the mixture at from 20° to 200°C, distilling off at a temperature below 200°C substantially all of the water formed in the reaction and a major portion of the unreacted dihydric alcohol, and heating the

distillation residue at from 70° to 200°C together with carbon dioxide.

18. The process of claim 1, wherein the temperature of the reaction mixture after the completion of the sulfurization reaction at from 110° to 200°C is kept at from 20° to 200°C to complete the metal addition reaction.

19. The process according to claim 1 wherein the weight ratio of the higher alcohol to the phenolic compound when said resultant mixture is heated at a temperature of from 110° to 200°C is at least 3.0.

20. The process according to claim 1 wherein the weight ratio of the higher alcohol to the phenolic compound when said resultant mixture is heated at a temperature of from 110° to 200°C is at least 10.5.

21. The process according to claim 1 wherein R is an alkyl group having from 1 to 50 carbon atoms.

22. The process according to claim 1 wherein said phenolic compound is selected from the group consisting of phenol, butylphenol, amylphenol, octylphenol, dioctylphenol, nonylphenol, dinonylphenol, dodecylphenol, cetylphenol, higher alkyl phenols having groups derived from olefin polymers, and mixtures thereof.

23. The process according to claim 22 wherein said olefin polymer contains from 9 to 125 carbon atoms.

24. The process according to claim 22 wherein said olefin polymer contains from about 3,500 to 7,000 carbon atoms.

25. The process according to claim 1 wherein said elementary sulfur is used in an amount at a level of from 1.0-3.5 g atoms per mole of said phenolic compound.

26. The process according to claim 1 wherein said higher alcohol has from 9 to 18 carbon atoms.

27. The process according to claim 1 wherein said resultant mixture is heated at a temperature of from 120° to 190°C.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,725,381 Dated April 3, 1973

Inventor(s) Yoshinori Sakai et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In The Specification:

Abstract - line 4	"oxide of" should be -- oxide or --
Column 3, line 10	insert -- of -- after "amount"
Column 4, line 17	"700% to" should be -- 700% of --
line 18	after "theoretical" insert -- amount --
line 52	after "increased" insert -- to --
line 54	before "much" insert -- a --
Column 5, line 9	"poybutylene" should be -- polybutylene --
Column 6, line 1	delete "10.5 times or higher to" and substitute -- of at least 10.5 times --

Signed and sealed this 28th day of January 1975.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,725,381 Dated April 3, 1973

Inventor(s) Yoshinori Sakai et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In The Specification:

Column 1, line 24 "containing a" should be -- containing an --

line 26 "radial" should be -- radical --

line 35 "requires" should be -- required --

line 57 "200C" should be -- 200°C --

Column 2, line 13 "overbased" should be --over-based --

line 19 "Process" should be -- Processes --

Column 3,

line 58 after "calcium" insert -- oxide --

Column 4, line 5 "The" should be -- These --

line 28 "untreated" should be -- unreacted --

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,725,381 Dated April 3, 1973

Inventor(s) Yoshinori Sakai et al Cont'd 2

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

line 37 "more to" should be -- more of --

line 45 "500%" should be -- 600% --

line 52 "more to" should be --more of --

Column 5, line 6 "nonyphenol" should be -- nonylphenol --

line 28 after "will" insert -- be --

line 34 before "atoms" insert --carbon --

line 62 "alcohols" should be -- alcohol --

Column 5, line 67 delete "as much as"

Column 6, line

line 39 before "art" insert -- prior --

Column 7, line 18 "carries" should be -- carried --

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,725,381 Dated April 3, 1973

Inventor(s) Yoshinori Sakai et al Cont'd 3

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

line 20 after "150°C" insert -- or of from 155 to 200°C --

line 38 "process" should be -- proceed --

line 39 after "addition" insert -- usually --

Column 8, line 25 "220°C" should be -- 200°C --

line 39 "reaction" should be -- react --

line 39 "ear" should be -- earth --

Column 9, lines 60-61 "p-octyphenol" should be -- p-octylphenol --

Column 11, line 59 after "give" insert -- a --

line 66 "gellike" should be -- gel-like --

Column 12, line 1 "Kg" should be -- kg --

line 13 "217°F" should be 210°F --

line 18 "of that" should be -- of the --

line 43 "has" should be -- had --

line 44 before "a total" insert -- and --

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,725,381 Dated April 3, 1973

Inventor(s) Yoshinori Sakai et al Cont'd 4

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

line 57 "has" should be -- had --

Column 13, line 37 change "to" to -- based on --

line 37 after "theoretical" insert -- amount --

In The Claim:

Column(13) line 44 after "reacting" insert -- a --

line 59 insert a comma (,) after "3"

line 66 "mold" should be -- mol --

Column 14, line 2 after "having" insert -- from --

line 2 change "nine" to -- 9 --

line 43 change "n" to -- in --

Signed and sealed this 25th day of June 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents