BASIC ALKYLYNE AMINE AND SULFUR BRIDGED ALKYLPHENOXIDES FOR USE IN LUBRICATING OILS


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U.S. Cl. 252—42.7

7 Claims

ABSTRACT OF THE DISCLOSURE

Novel dispersant detergents are provided by combining, at an elevated temperature, a sulfurlzed alkylphenoil and a Mannich base—prepared from formaldehyde, alkylphenol, and a lower alkyl monoamine—in the presence of an alkaline earth metal base and a liquid hydroxyl compound, so as to prepare the alkaline earth metal salt of a chemically combined sulfurlzed alkylphenol and Mannich base. The compositions which are detergent dispersants also provide antioxidant activity and alkalinity reserve.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 97,300, filed Dec. 11, 1970, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

Lubricating oils used under the severe conditions of diesel engines are highly compounded so as to provide neutralization of acids derived from the sulfur in the fuel and oxidation of hydrocarbons, both of the fuel and oil; dispersancy so as to maintain sludge-forming precursors dispersed in the oil; improved wear protection and oiliness properties; as well as enhancing other attributes of the oil. In addition to the requirements normally attendant to a diesel lubricating oil, those oils which find use in railroad diesel engines have the additional factor of not being corrosive or reactive to silver. Silver bearings are used in a preponderant number of diesel engines today.

The desirability of having a single additive providing multifunctional properties is evident in the efficiency and economies in the manufacturing and using of a single additive as compared to a plurality of additives. However, because of the severe operating conditions under which a lubricating oil performs in diesel engines, it is frequently found that additives, while effectively performing a particular function, will tend to degrade and enhance deposit formation. Therefore, in designing any particular additive, it is essential not only that it fulfill the function(s) for which it has been designed, but that it be stable under the conditions of use or degrade slowly to materials which do not enhance deposit formation.

Description of the prior art


SUMMARY OF THE INVENTION

New detergent dispersant phenates having alkalinity reserve and antioxidant activity are prepared by the simultaneous neutralization of a sulfurlzed alkylphenol and a Mannich base prepared from a lower alkyl amine, an alkylphenol and formaldehyde. The neutralization is carried out at elevated temperatures with an alkaline earth metal base in the presence of a hydroxyl solvent under conditions to minimize the loss of amine nitrogen.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

The compositions of this invention are the reaction products of an alkaline earth metal base, oxide or hydroxide, a Mannich base—prepared from formaldehyde, alkylphenol, and a primary lower alkyl amine—and a sulfurlzed alkylphenol. The reaction is carried out at elevated temperatures so that molecular bonds are formed between the Mannich base and the sulfurlzed alkylphenol in addition to those bridges bonds created by the divalent alkaline earth metal.

The product as formed (independent of any diluent) will have an alkalinity value (ASTM Test—D2896) in mg. KOH/g. in the range of 130 to 450, more usually about 175 to 400. The product will provide in elemental analysis from about 4 to 12, more usually from about 5 to 10, weight percent calcium, at least about 0.1 to 5, more usually from about 0.5 to 4, weight percent nitrogen, and from about 0.8 to 10, more usually from about 2 to 8, weight percent sulfur. In a 100 neutral oil, (100 being the viscosity at 100° F. in SUS) at an alkaline earth metal concentration of 0.88 normal (3.5 weight percent for Ca), the viscosity at 210° F. will normally be in the range of about 200 to 3,000 SUS, more usually in the range of 500 to 1,500 SUS.

The compositions of the subject invention are complex in nature. It is believed that a substantial proportion of the composition corresponds to one of the following formulae:

1. \( O - (A - B) - O \)

2. \( O - (B - A) - B \)
wherein:

\[
\begin{align*}
A & = \left\{ \begin{array}{c}
\text{CH-N-OH, R} \\
\text{R'}
\end{array} \right\} \\
B & = \left\{ \begin{array}{c}
\text{O-} \\
\text{(S)}
\end{array} \right\}
\end{align*}
\]

\(a = 1 \text{ to } 3;\)
\(b = 0 \text{ to } 1;\)
\(x = 1 \text{ to } 20, \text{ primarily } 4 \text{ to } 9;\)
\(y = 1 \text{ to } 10, \text{ primarily in the range } 1 \text{ to } 5, \text{ preferably } 2 \text{ to } 4;\)
\(n = 1 \text{ to } 5, \text{ more usually } 1 \text{ to } 3;\)
\(R = \text{ a saturated aliphatic hydrocarbon, either branched}-\)
\(\text{or straight-chain, having from 8 to 36 carbon atoms,}\)
\(\text{more usually from 10 to 24 carbon atoms, the average number of carbon atoms generally being in the range}\)
\(\text{of about } 10 \text{ to } 20;\)
\(R' \text{ is lower alkyl, usually of from } 1 \text{ to } 3 \text{ carbon atoms,}\)
\(\text{and preferably of 1 carbon atom, namely, methyl.}\)

The ratio over the entire composition of the equivalents of alkylphenol from the Mannich base to equivalents of alkylphenol from the sulfurized alkylphenol will normally be 0.2–2:1, more usually 0.3–3:1, and preferably 0.3–2:1.

The remaining valences of the oxygen atoms are satisfied by an alkaline earth metal. These metals are calcium and barium, preferably calcium. Both valences of the metal may be satisfied by the phenoxide or one valence by the phenoxide and the other valence by an alkoxide or hydroxide, the group varying with the hydroxyllic solvent employed and the proportion of alkaline earth metal used in the reaction. A few of the phenoxide groups, not exceeding 10 mole percent, may be bonded to hydrogen, depending on the amount of excess of alkaline earth metal present.

The reactions of this invention are prepared by combining in a suitable reactor the Mannich base and sulfurized alkylphenol in an equivalent ratio (based on phenol) in the range of 0.2–5:1, more usually 0.3–3:1. In addition to the above reactants are included an alkaline earth metal oxide or hydroxide, preferably hydroxide, and a hydroxyllic solvent, usually ethylene glycol.

The amount of alkaline earth metal base will depend on the method of preparation of the sulfurized alkylphenol. To the degree that an alkaline earth metal base was employed during the preparation of the sulfurized alkylphenol, the added amount of alkaline earth metal base will provide a total of at least one equivalent of alkaline earth metal present per equivalent of alkylphenol present, usually not exceeding 1.75 equivalents, and more usually not exceeding 1.5 equivalents of alkaline earth metal per equivalent of phenol present.

The amount of the hydroxyllic solvent will vary with the particular solvent employed. Ethylene glycol, propylene glycol, and methanol are examples of suitable solvents. Since ethylene glycol is the preferred solvent, only its use will be discussed in detail. The amount of ethylene glycol employed will normally be from about 5 to 35 weight percent, preferably from about 7 to 20 weight percent, of the total reaction mixture.

In addition to the ethylene glycol, inert hydrocarbon diluent may also be present. These inert diluents may serve to aid in the handling of the reactants, lowering the viscosity of the reaction mixture, and enhancing the ease of isolation of the product. In view of the use of the subject compositions, mineral oils of lubricating viscosity may be employed and the product isolated as a solution in the mineral oil. Normally, the inert diluent will be present in the reaction mixture, if at all, in amounts of from 3 to 65 weight percent more usually 5 to 50 weight percent of the total reaction mixture.

Conveniently a small amount of an antifoaming agent or foaming suppressant may be employed. The foam suppressant will normally be present in the reaction mixture in amounts of 1x10^-2 to 1x10^-4 weight percent. Foaming suppressants are conventional and need not be exemplified here.

The reaction is conveniently carried out by combining the sulfurized alkylphenol, the Mannich base, the alkaline earth metal oxide or hydroxide, and ethylene glycol. As already indicated, an inert diluent may also be present.

Preferably, prior to the addition of the ethylene glycol, the mixture is heated to at least 90°C, but below the temperature at which the reaction is to be carried out, normally below 140°C.

After addition of the ethylene glycol, the temperature is raised so as to distill water overhead, removing the water of reaction. The temperature is raised, not to exceed 200°C. The pressure is reduced to permit the distillation of ethylene glycol. Usually, the temperature during removal of water will range from 125° to 160°C, while the temperature during removal of ethylene glycol will range from 140° to 200°C, preferably from 160° to 180°C. The pressure will vary, depending on the temperature and rate of distillation desired. The reduced pressure may vary from about 0.01 to 0.8 atmosphere.

The time required for the removal of water will usually be from about 30 minutes to 3 hours. The time for the removal of ethylene glycol will normally be about 30 minutes to 9 hours. The time for the reaction, that is, from the initial removal of water to substantially complete removal of ethylene glycol, will vary from about 1 hour to 6 hours. The time, while not a critical factor, should not be unduly protracted, and will depend on the capacity of the equipment, the amount of reactants, the degree of foaming and the ability to control the temperature and rate of removal of distillates.

When no further ethylene glycol comes over, the reaction mixture may be cooled. Depending on the presence and amount of inert diluent, the temperature should preferably be maintained above about 150°C prior to sufficient dilution with a convenient solvent. The mixture can become extremely viscous, and solution into a solvent is difficult below a temperature of about 150°C. Any convenient solvent may be used, but in view of the intended use, normally a hydrocarbonaceous lubricating oil will be used as the diluent. Depending on the end use, various hydrocarbonaceous lubricating oils may be employed. As diluted, the product is ready to be employed, after filtration, as a concentrate for formulating finished lubricating oils.

The various reactants will now be considered. The first and simplest reactant is the alkaline earth metal oxide or hydroxide. As already indicated, these are calcium and barium, preferably calcium. With calcium, normally calcium hydroxide will be employed.

Sulfurized alkylphenols are well known materials for use in lubricating oils. The method of preparation of the sulfurized alkylphenols is not critical to this invention. The sulfurized alkylphenol should have at least about 4 weight percent sulfur and not more than about 20 weight percent sulfur, more usually from about 8 to 18 weight percent sulfur. Preferably, there will be at least 0.5, and not more than about 12 weight percent sulfur, based on the weight of the sulfurized phenol composition present which is not involved in bridging or is involved in bridges having at least 3 sulfur atoms. Usually, there will be
present about 1 to 9 weight percent sulfur, based on the weight of sulfurized phenol composition which is in a form for a bridging reaction. The sulfurized alkylphenols will, for the most part, have the following formula:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
R_2 & \quad \text{N}
\end{align*}
\]

wherein \(R_2\) is alkyl of from 8 to 36 carbon atoms, more usually of from 10 to 24 carbon atoms with the average number of carbon atoms being in the range of about 10 to 20, \(x^2\) is an integer of from 1 to 9, more usually of from 1 to 5, averaging over the entire composition in the range of about 2 to 4, and \(n^2\) is an integer of from 1 to 5, more usually of from 1 to 3. There may be small amounts, not more than about 10 weight percent, of sulfurized phenol having \(x^2\) greater than 9.

The aliphatic hydrocarbon groups designated \(R^2\) may be in the ortho, meta, or para positions, but will predominate in the meta or para positions. Since branched-chain alkyl groups tend to minimize the amounts of ortho-substituted phenols, the branched-chain alkyl groups are preferred. However, it should be realized that to some extent the alkyl groups are in the ortho position, and ortho-substituted phenols act as chain terminals in the copolymerization of sulfur and alkylphenol.

The sulfurized alkylphenol can be prepared by combining alkylphenol, sulfur, calcium oxide, or calcium hydroxide and glycol at an elevated temperature, driving off the water and hydrogen sulfide, followed by isolation of the sulfurized alkylphenol. See, for example, U.S. Patent No. 2,989,466. Sulfur monochloride may also be used to prepare sulfurized alkylphenols, frequently employing a Friedel-Crafts catalyst to aid the reaction. Various methods of preparing sulfurized alkylphenols may be found in U.S. Patents Nos. 2,362,289, 2,451,345, 2,744,083, and 3,367,867.

The Mannich bases which are employed are prepared by combining at elevated temperatures, an alkylphenol, formaldehyde, and a primary lower alkylamine, preferably of from 1 to 3 carbon atoms, and particularly preferred, methyl amine. A method for preparing the Mannich bases may be found in copending application Ser. No. 22,452, filed on Mar. 25, 1970. U.S. Patent No. 3,454,497 describes an additional method for preparing Mannich bases employing primary amines.

The Mannich bases will, for the most part, have the following formula:

\[
\begin{align*}
\text{R}^1 & \quad \text{OH} \\
\text{R}^2 & \quad \text{CH}_{2}\text{NH}_{2}\text{R}^3
\end{align*}
\]

wherein \(R^1\) is lower alkyl, usually of from 1 to 3 carbon atoms, and preferably of 1 carbon atom, methyl, \(R^2\) is saturated aliphatic hydrocarbon of from 8 to 36 carbon atoms, more usually of from 10 to 24 carbon atoms, and normally having an average number of carbon atoms in the range of from 10 to 20, \(x^2\) will range from 1 to 19, usually averaging in the range of 4 to 9. There may be small amounts, less than 10 weight percent, of Mannich bases having \(x^2\) greater than 19. The average over the entire composition will normally be in the range of 3 to 9, with more than 50 weight percent of the composition having \(x^2\) equal to 3, or higher.

The Mannich base will normally be prepared from alkylphenols having less than 25 mole percent, preferably less than 20 mole percent ortho substitution. The Mannich base in the invention will have less than 20, usually less than 10, number percent of attachment of the Mannich amine at the position para to the hydroxyl group of the phenol.

The Mannich base (undiluted) will have at least 2 weight percent nitrogen and normally not more than about 5 weight percent nitrogen, the amount of nitrogen normally being in the range of about 2.2 to 4.0. The average molecular weight, as determined by osmometry, will be at least 600, more usually at least 700, and normally not exceed about 5,000.

The following examples are offered by way of illustration and not by way of limitation. (All parts are by weight, unless otherwise indicated.)

**EXAMPLE 1**

Into a reaction vessel are introduced 8,825 parts of sulfurized alkylphenol (prepared as described in Example A), 10,350 parts of a Mannich base (prepared as described in Example B) as a 60 weight percent solution in a mid-continent 100 neutral oil, 2 parts of DC-200 foam inhibitor, and 1,640 parts of calcium hydroxide. The mixture is heated at 250-275°F. and 5,150 parts of ethylene glycol added. The pressure is then reduced to 20” mercury and the mixture heated to 300°F. over a period of 50–70 minutes while water is removed overhead. When substantially all of the water is removed, the temperature is then raised to 375°F. over a period of two to three hours. The pressure is concomitantly reduced so that the maximum vacuum is reached at about the time the temperature reaches 340°F. The final pressure on the kettle is not greater than 50 millimeters of mercury. When the temperature of 370°F. is achieved, this temperature and the maximum vacuum is held for 30 minutes.

The mixture is then cooled rapidly to 300°F. and nitrogen introduced into the system to atmospheric pressure. The mixture is then charged 4,500 parts of 100 neutral oil and the solution mixed for 30 minutes while maintaining the temperature at about 250°F. The product may then be isolated.

The above product will have about 4.2 weight percent calcium and a viscosity of about 4,000 SUS at 210°F.

**EXAMPLE A**

Into a reaction vessel are introduced 18,100 parts of polypropylene (prepared from polypropylene of from about 12 to 15 carbon atoms), 750 parts of calcium oxide and 4,620 parts of sulfur, the temperature of the mixture being maintained at 220°F. The temperature is then raised to 265–275°F. and 580 parts of ethylene glycol charged. Hydrogen sulfide begins to evolve and a low rate nitrogen purge is then begun over the top of the reactor. The temperature is slowly raised to 335–340°F. and the temperature maintained for a period of 6 hours. At the end of this time, the mixture is cooled to about 225–250°F. and the product may be isolated.

**EXAMPLE B**

Into a reaction vessel is introduced 60.4 parts of polypropylene (prepared from polypropylene of from about 12 to 15 carbon atoms) and the system degassed and purged with nitrogen. After the purging is completed, 17.9 parts of isobutyl alcohol and 14.5 parts of paraformaldehyde are added while the mixture is agitated. To the mixture, then added 7.2 parts of liquid methyl amine, the addition requiring 3 hours. The temperature, during the addition, is maintained at 120–150°F.

After completion of the addition of the methyl amine, the mixture is stirred for an additional 15 minutes and
the vessel vented. The temperature is then raised to 190°F, the vessel closed, and the temperature raised to 260°F. The temperature is maintained for a period of 7 hours, while a pressure of 20 ps.i.g. is maintained. The product may then be isolated by washing with water and then distilling the isobutyl alcohol.

If desired, the product may be diluted with an inert diluent for convenient handling. The product is then heated in vacuo for about 30 minutes at 300°F, following which it is ready for use in the final reaction.

**EXAMPLE 2**

Into a reaction vessel were introduced 8,643 grams of sulfurized alkylphenol (unfiltered), 9,255 grams of the Mannich base, as a 66 weight percent solution in 100 neutral oil, and 1,618 grams of calcium hydroxide, followed by the addition of 5,122 grams of ethylene glycol and 4 grams of DC-200, a foaming suppressant.

(The sulfurized alkylphenol was prepared as described in Example A, filtered, and had the following specifications (neat): The alkylphenol was polypropylphenol having an alkyl group of from 12 to 15 carbon atoms; alkalinity value mg. KOH/g. 63.6; percent Ca, 2.27; percent S, 14.99; viscosity at 210°F, SUS, 2740.)

The Mannich base was prepared from polypropyl alkylphenol (polypropylene of from 12 to 15 carbon atoms) as described in Example B. The product had the following specification, as a 66.7 weight percent solution in a mid-continent 100 neutral oil: percent N, 2.74; alkalinity value mg. KOH/g, 109; viscosity at 210°F, SUS, 425.

The mixture was heated rapidly to 265°F and a 10" Hg vacuum applied, water and hydrogen sulfide being removed overhead. The pressure was decreased and the temperature raised over a period of 4 hours and 20 minutes, the final temperature being 380°F, and the final vacuum about 48 mm. Hg. During this time, water and ethylene glycol were taken overhead. The mixture was cooled to 275°F, the vacuum broken with the introduction of nitrogen and when the temperature had fallen to about 260°F, 5,092 grams of a mid-continent 100 neutral oil was added as diluent.

The product as an oil solution had an alkalinity value of 147 mg. KOH/g, percent N, 0.75; percent S, 3.2; and percent Ca, 4.2. After some difficulty, the product was diluted further with mid-continent 100 neutral oil and filtered using a mixture of Celite 573 and Celite 545. The filtered product weighed 15,457 grams. Percent N, 0.60, percent Ca, 3.35, percent S, 3.12.

**EXAMPLE 3**

Into a reaction vessel were introduced 427 grams (1.28 equivalents) of sulfurized alkylphenol and 454 grams (0.93 equivalent) of the Mannich base described in Example 2 as a 66.7 weight percent active solution, the mixture heated to 95°C. and 253 grams of ethylene glycol and 80 grams (2.16 equivalents) of calcium hydroxide added. The pressure was reduced to 10" vacuum and water collected overhead as the temperature was raised to 125°C. The temperature was then raised to 150°C over a 55-minute period, followed by slowly reducing the pressure to 25 mm. Hg, while slowly raising the temperature to 182°C. The temperature was maintained for 15 minutes, and then the reaction mixture was allowed to cool, nitrogen being introduced to break the vacuum. The product was then diluted with 300 grams of a mid-continent 100 neutral oil. The oil solution was then filtered through Celite, the filtered product weighing 1,105 grams.

Analyse (percent): Ca, 4.43, 4.24; N, 0.82, 0.82; S, 3.56. Alkalinity value, mg. KOH/g., 152.5, 151.4.

The sulfurized alkylphenol employed above was prepared as described in Example A and had the following specifications: percent S, 14.9; alkalinity value mg. KOH/g., 62.7; percent Ca, 2.16, viscosity at 210°F, SUS, 2,435.

A number of additional examples were carried out following substantially identical procedures, with minor variations, except for variation in the ratio of sulfurized alkylphenol and Mannich base. Both the sulfurized alkylphenol and Mannich base were obtained from the same batch preparation. The following table indicates the amounts of material employed, and the specifications in the final product. All of the specifications indicated are based on a composition which is 63 weight percent active in a mid-continent 100 neutral oil.

<table>
<thead>
<tr>
<th>Example</th>
<th>Sulfurized alkylphenol, &amp;g.</th>
<th>Mannich base, &amp;g.</th>
<th>Ethylene glycol, &amp;g.</th>
<th>Ca</th>
<th>S</th>
<th>Percent Alkalinity value, mg. KOH/g.</th>
<th>N</th>
<th>Sulfurized alkylphenol, Oil</th>
<th>Mannich base, Oil</th>
<th>Ethylene glycol, Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>234</td>
<td>800</td>
<td>322</td>
<td>145</td>
<td>75</td>
<td>328, 1.67, 1.05, 4.07, 4.07, 3.30, 2.10</td>
<td>155</td>
<td>75</td>
<td>152.5, 151.4</td>
<td>152.5, 151.4</td>
</tr>
<tr>
<td>2</td>
<td>1,092</td>
<td>500</td>
<td>488</td>
<td>45</td>
<td>80</td>
<td>650, 0.42, 4.34, 4.34</td>
<td>46</td>
<td>80</td>
<td>160.1</td>
<td>160.1</td>
</tr>
<tr>
<td>3</td>
<td>854</td>
<td>1,300</td>
<td>458</td>
<td>145</td>
<td>109</td>
<td>164, 1.41, 3.74, 3.74</td>
<td>161</td>
<td>1.41</td>
<td>170.6</td>
<td>170.6</td>
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<tr>
<td>4</td>
<td>384</td>
<td>1,100</td>
<td>344</td>
<td>109</td>
<td>109</td>
<td>278, 1.61, 1.39, 3.78, 3.78, 1.98, 1.98</td>
<td>162.8</td>
<td>1.98</td>
<td>197.4</td>
<td>197.4</td>
</tr>
<tr>
<td>5</td>
<td>668</td>
<td>500</td>
<td>844</td>
<td>109</td>
<td>109</td>
<td>480, 0.61, 0.61, 4.08, 4.08, 4.70, 4.04</td>
<td>148.7</td>
<td>4.70</td>
<td>197.4</td>
<td>197.4</td>
</tr>
</tbody>
</table>

1 66.7 weight percent active mid-continent 100 neutral oil.
2 Added at completion of reaction.
3 Analysis carried out on diluted product.

**EXAMPLE 9**

Into a reaction vessel were introduced 427 grams of sulfurized alkylphenol prepared as follows.

Into a reaction vessel were added 3011 grams of polypropylene phenol (polypropylene of from 12 to 15 carbon atoms), the mixture heated to 150°F and 125 grams of calcium oxide added. The temperature was raised to 270°F, when 769 grams of sulfur were charged, followed by the addition of 96 grams of ethylene glycol. The mixture refluxed for about 10 minutes, with hydrogen sulfide coming off. The temperature was continuously increased until 340°F was reached, the temperature was then maintained for 6 hours at which time the reaction mixture was allowed to cool to room temperature and introduced into an inert atmosphere. The product weighed 3666 grams, an aliquot was taken for analysis and filtered. Analysis: percent S, 14.57. Alkalinity value, mg. KOH/g, 61.39 which is equal to 2.19 percent Ca.

To the 427 grams of sulfurized alkylphenol was added 454 grams of the Mannich base described in Example 2, the mixture heated to 200°F, at which time 80 grams of calcium hydroxide and 253 grams of ethylene glycol were charged. The temperature was then raised over a period of about 1 hour and 15 minutes to 360°F while the pressure was slowly reduced to a final pressure of 40 mm. Hg. After holding the temperature and pressure for about 10 minutes, the mixture was then allowed to cool to 250°F, a nitrogen atmosphere introduced and 300 grams of a mid-continent 100 neutral oil added. The final product weighed 1185 grams. Analysis (percent): N, 0.71, 0.72; S, 3.19; Ca, 4.01. Alkalinity value, mg. KOH/g, 134.9, 133.9.

A number of sulfurized alkylphenols were prepared by the process described in Example A, where the sulfur to alkylphenol ratio was varied. These compositions were then combined with Mannich base as prepared in Example B, substantially following the procedure of Example 1. The table below indicates the sulfur to alkylphenol ratios, the analysis of the product, the analysis of the Mannich base and the analysis of the final product.
TABLE II

<table>
<thead>
<tr>
<th>Example</th>
<th>Resistant sulfur parts</th>
<th>Product</th>
<th>Sulfurized alkylphenol Parts</th>
<th>Sulphurized alkylpheno</th>
<th>Mannich Base Parts</th>
<th>Analysis S</th>
<th>A.V. mg. KOH/g.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>269</td>
<td>6.32</td>
<td>81.2</td>
<td>378</td>
<td>475</td>
<td>0.84</td>
<td>0.82</td>
<td>4.18</td>
<td>1.21</td>
<td>162</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>284</td>
<td>7.69</td>
<td>76.6</td>
<td>380</td>
<td>475</td>
<td>0.83</td>
<td>0.82</td>
<td>4.18</td>
<td>1.21</td>
<td>162</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>476</td>
<td>11.97</td>
<td>72.2</td>
<td>407</td>
<td>475</td>
<td>0.87</td>
<td>0.88</td>
<td>4.36</td>
<td>1.70</td>
<td>165</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>13</td>
<td>768</td>
<td>18.60</td>
<td>67.4</td>
<td>427</td>
<td>475</td>
<td>0.80</td>
<td>0.78</td>
<td>4.28</td>
<td>3.37</td>
<td>164</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>14</td>
<td>970</td>
<td>25.01</td>
<td>63.3</td>
<td>448</td>
<td>475</td>
<td>0.85</td>
<td>0.83</td>
<td>4.50</td>
<td>3.14</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>121</td>
<td>51.72</td>
<td>70.5</td>
<td>380</td>
<td>475</td>
<td>0.85</td>
<td>0.83</td>
<td>4.50</td>
<td>3.14</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>16</td>
<td>138</td>
<td>72.97</td>
<td>75.6</td>
<td>380</td>
<td>475</td>
<td>0.85</td>
<td>0.83</td>
<td>4.50</td>
<td>3.14</td>
<td>147</td>
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<td></td>
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<td>17</td>
<td>278</td>
<td>77.95</td>
<td>73.6</td>
<td>604</td>
<td>505</td>
<td>0.66</td>
<td>0.66</td>
<td>4.38</td>
<td>3.81</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Combined with the sulfur were 12% parts of CaO, 2,400 parts of alkyl phenol (alkyl is propylene of from 12 to 16 carbon atoms), and 96 parts of ethylene glycol.
2. A.V. percentage value (ASTM D-299).
3. Preparation as indicated in Example 4.
4. In addition to the sulfurized alkyl phenol and Mannich base used 25 parts of ethylene glycol, 80 parts of calcium hydroxide and 800 parts of a mid-continent 100 neutral oil.
5. Analysis carried out on distilled products.

EXAMPLE 18

Into a reaction flask fitted with nitrogen bubbler was introduced 100 grams of 2,2'-bis(1-hydroxy-4-polypropylene-phenyl)-disulfide (polysulfide of from 12 to 15 carbon atoms) as a 75 wt. percent solution in oil and 150 grams of the Mannich base prepared as described in Example B as a 66.7 wt. percent active solution in a mid-continent 100 neutral oil (alkalinity value mg. KOH/g. 108; percent N, 2.74) and the mixture heated to 100 °C. While maintaining a nitrogen atmosphere. To the reaction mixture was then added 18 g. of calcium hydroxide, 29 g. of ethylene glycol and one drop of DC 200. The temperature was then raised to 150 °C. and the pressure dropped to 200 mm. Hg and these conditions maintained for 30 minutes. The pressure was then reduced to 50 mm. Hg, the temperature raised to 180 °C. and maintained for 15 minutes. At the end of this time, the mixture was cooled to 100 °C. and filtered through a 50/50 mixture of Celite 512 and Dicalite 573. The filtration was slow. Analysis (percent): N, 12.0; Ca, 3.52; A.V. mg. KOH/g., 147.

The compositions of this invention find particular use in lubricating oils where not only detergent and dispersancy are desirable, but also acid neutralization capability and antioxidant activity. The compositions of this invention can be used with various base oils which find use as lubricating oils. Oils of lubricating viscosity have viscosities in the range of about 30 to 50,000 SUS (Saybolt Universal Seconds) at 100 °F. Normally, the oils which find use in this invention will have viscosities at 210 °F. in the range of about 20 to 150 SUS, more usually from about 60 to 120 SUS. The hydrocarbon lubricating oils may be derived from natural sources and be paraffinic, naphthenic, or aromatic based on mixtures thereof. Alternatively, synthetic hydrocarbon oils may be used.

The compositions of this invention may also find use in nonhydrocarbon synthetic oils such as esters, silicates, etc. The various oils may be used together whenever miscible or made to be by mutual solvents.

The compositions of this invention when formulated as concentrates, will normally be from about 15 to 70 weight percent, more usually from about 30 to 60 weight percent.

When used in formulations, depending on the particular formulation, the amount of the subject composition will generally vary from about 5 to 400 m/M./kg, based on metal, more usually from about 8 to 75 M./kg. based on metal. Usually, in a railroad oil formulated combination, the alkalinity value is at least 5, more usually of at least 6 mg. KOH/g. and not more than about 15 mg. KOH/g.

Various other additives may also be present in the formulation. Of particular interest for use in combination with the subject additives are sulfurized aliphatic hydrocarbons. These compositions are well known in the art and tend to have from about 16 to 50 carbon atoms and vary from about 15 to 25 weight percent sulfur. These additives will be present in from 0.05 to 0.75 weight percent.

In addition to the sulfurized hydrocarbons, it is also advantageous to employ nonash-containing detergents and dispersants, to provide a low ash composition. These ashless detergent dispersants are primarily aliphatic polyols of from 2 to 6 hydroxyl group or alkylene polyamines (alkylene of from 2 to 3 carbon atoms) having from 3 to 5 amine nitrogen atoms, either directly bonded to an aliphatic hydrocarbon group of from about 30 to 200 carbon atoms, more usually from 50 to 125 carbon atoms, or indirectly to an acyl group, such as succinyl, phospho-acyl, carboxyl, etc., where the acyl group has a hydrocarbon substituent and forms ester or polyester with the alcohols, and an amide or imide, e.g., succinimide, link to the alkylene polyamine. See U.S. Pat. Nos. 3,522,179, 3,331,776, 3,219,666 and 3,202,768, which disclose polyisobutylene succinimides of alkylene polyamines (polyisobutyl of from 50 to 200 carbon atoms; alkylene polyamines-alkylen- of from 2 to 3 carbon atoms and polyamine of from 2 to 5 nitrogen atoms; succinimides to alkylene polyamines being 1-2:1). The ashless detergents will generally be present in from about 2.5 to 10 weight percent, more usually from about 3 to 8 weight percent.

Other additives may also be present in minor amounts, such as additional ash-containing detergents, e.g. sulfonates, both neutral and overbased, phosphonates, both neutral and over-based, corrosion inhibitors, oiliness agents, pour point depressants, viscosity index improvers, etc.

In order to demonstrate the effectiveness of the subject compositions, a number of bench tests and engine tests were carried out, the results being provided in Table III infra.

The first test to be discussed is referred to as the Oxidation Test to determine antioxidant activity. To 25 grams of the test oil is added 0.26 cc. of a solution having 2268 p.p.m. of copper, 6236 p.p.m. of iron, 567 p.p.m. of manganese, 4535 p.p.m. of lead, and 4535 p.p.m. of chromism, all as their naphthenates, providing a distribution of metals which would be expected to be found in a used crankcase oil from a General Motors D-71 diesel engine. The oil sample to be tested is placed at 340 °F, with stirring in an oxygen atmosphere and the percent increase in viscosity at 100 °F. in ten hours determined.

The subject compositions were formulated in a 70 V.I. SAE 40 oil to simulate a commercial formulation. In the oil were employed 59 m/M./kg. based on calcium of the test composition, 6 weight percent a bis(polyisobutylene succinimide) of tetraethylen pentamc (mixed polyisobutyl of about 640 and 1000 number average molecular weight), 22 M./kg. based on calcium of...
calcium mahogany sulfonate (1.67 wt. percent Ca), 0.3 wt. percent of sulfurized paraffin having 17.5 wt. percent sulfur, and 0.025 wt. percent of terephthalic acid.

The second test to be discussed is the silver thrust washer test. In this test, a silver test piece is used made of fine silver, 99.9 percent pure, soldered to a backing of soft steel. Both silver and backing are nominally \( \frac{3}{16} \) in thickness. One end is rounded and the other is flat. A 0.01-inch deep and \( \frac{3}{16} \)-inch wide slot is cut across the center of each of the three raised silver surfaces.

In this time, the solution is divided between two 100 ml calibrated centrifuge tubes and then centrifuged at 2200 r.p.m. for 0.5 hour. The sediment is read and the average of the two readings taken. The results are reported as ml of sediment per 10 mg KOH/g. of sample and ml of sediment per 10 mg KOH/g. of sample due to amine nitrogen.

For the Oxidor B test and the silver thrust washer test, the formulated oil described previously was employed. For the sediment test the sample prepared as a 63 percent active solution in 100 neutral oil was employed. The following table indicates the results.

### Table III

<table>
<thead>
<tr>
<th>Example</th>
<th>Oxidation test percent increase in 10 hrs.</th>
<th>Silver thrust washer Watts</th>
<th>Sulfuric acid sediment, ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt. loss, mg. 45 min. 60 min.</td>
<td>Per 10 A.V. based on N</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>58.5</td>
<td>165</td>
<td>168</td>
</tr>
<tr>
<td>3</td>
<td>60.0</td>
<td>165</td>
<td>168</td>
</tr>
<tr>
<td>4</td>
<td>73.5</td>
<td>177</td>
<td>180</td>
</tr>
<tr>
<td>5</td>
<td>14.7</td>
<td>1.2</td>
<td>177</td>
</tr>
<tr>
<td>6</td>
<td>28.3</td>
<td>0.9</td>
<td>165</td>
</tr>
<tr>
<td>7</td>
<td>64.7</td>
<td>2.1</td>
<td>180</td>
</tr>
<tr>
<td>8</td>
<td>10.1</td>
<td>1.1</td>
<td>183</td>
</tr>
<tr>
<td>9</td>
<td>70.9</td>
<td>0.6</td>
<td>170</td>
</tr>
<tr>
<td>10</td>
<td>38.0</td>
<td>1.0</td>
<td>176</td>
</tr>
<tr>
<td>11</td>
<td>28.9</td>
<td>0.7</td>
<td>185</td>
</tr>
</tbody>
</table>

In order to demonstrate the subject compositions' activity under severe conditions in a diesel engine, a 180 BMEP test was carried out. The one-cylinder diesel engine employed has a bore of \( \frac{5}{16} \) and a stroke of \( \frac{3}{16} \). The brake horsepower is 55, and the engine is run at 7460 B.P.M. per minute and 1880 r.p.m., with the air temperature at 255°F., the outlet water temperature at 190°F., the oil to bearing temperature at 205°F. and a fuel which contains 1.0 weight percent sulfur. Using the formulation described previously, the test was run for 120 hours and the following results obtained.

### Table IV

<table>
<thead>
<tr>
<th>Grooves</th>
<th>Lands</th>
<th>Under head</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>77-7.4-5.8</td>
<td>260-70-55</td>
</tr>
<tr>
<td>3</td>
<td>90-9.2-5.8</td>
<td>65-35-35</td>
</tr>
<tr>
<td>4</td>
<td>92-8.6-5.8</td>
<td>285-45-49</td>
</tr>
<tr>
<td>5</td>
<td>64-3.1-5.7</td>
<td>55-30-135</td>
</tr>
<tr>
<td>6</td>
<td>94-14-6.9</td>
<td>310-100-81</td>
</tr>
<tr>
<td>7</td>
<td>17-2.9-0.5</td>
<td>50-35-35</td>
</tr>
</tbody>
</table>

In order to demonstrate the subject compositions' activity under severe conditions in a diesel engine, a 180 BMEP test was carried out. The one-cylinder diesel engine employed has a bore of \( \frac{5}{16} \) and a stroke of \( \frac{3}{16} \). The brake horsepower is 55, and the engine is run at 7460 B.P.M. per minute and 1880 r.p.m., with the air temperature at 255°F., the outlet water temperature at 190°F., the oil to bearing temperature at 205°F. and a fuel which contains 1.0 weight percent sulfur. Using the formulation described previously, the test was run for 120 hours and the following results obtained.

The above results demonstrate the excellent effectiveness of the subject compositions under a wide variety of conditions. The subject compositions provide low sediment when neutralized in sulfuric acid. In addition, they significantly reduce the wear loss with silver bearings. Also of importance, under extremely severe conditions at high temperatures in a diesel engine, they are able to maintain at low level of deposits. In addition, they provide excellent antioxidant activity, minimizing viscosity increase in lubricating oils and are able to neutralize gross amounts of acids.

What is claimed is:

1. A composition of matter comprising in an admixture a major amount of an oil of lubricating viscosity and
from 5 to 400 millimoles per kilogram of oil based on calcium or barium of the reaction product of
(1) a Mannich base of the formula:

\[
\text{R}^4 \quad \text{N} \quad \text{R}^3 \quad \text{R}^1
\]

wherein:
- \( \text{R}^4 \) is a lower alkyl having from 1 to 3 carbon atoms;
- \( \text{R}^3 \) is a saturated aliphatic hydrocarbyl having from 8 to 36 carbon atoms,
- \( x \) is an integer from 1 to 19;

with (2) a sulfurized alkylphenol of the formula:

\[
\text{H} \quad \text{O} \quad \text{R}^2 \quad \text{R}^1
\]

wherein:
- \( \text{R}^2 \) is an alkyl of 8 to 36 carbon atoms,
- \( n \) is an integer from 1 to 5, and
- \( y \) is an integer from 1 to 9;

and
(3) a calcium or barium base;

wherein the ratio of equivalents of alkylphenol from said Mannich base to equivalents of alkylphenol from said sulfurized alkylphenol in said reaction product is from 0.2 to 5:1, the said calcium or barium base is used in an amount sufficient to provide a total of 1 to about 1.75 equivalents to said calcium or barium base per equivalent of alkylphenol.

The composition defined in claim 1 wherein said reaction product when admixed with a 100 neutral oil at a concentration of 0.88 formal of calcium or barium has a viscosity at 210° F. in the range of 200 to 3,000 SUS.

The composition defined in claim 1 wherein said calcium or barium base is calcium hydroxide, said reaction product has an alkalinity value in the range of 130 to 450 and contains from 4 to 12 weight percent calcium and 0.1 to 5 weight percent nitrogen.

The composition defined in claim 3 wherein said \( \text{R}^4 \) is methyl.

The composition defined in claim 3 wherein \( \text{R}^2 \) and \( \text{R}^3 \) are polypropyl of about 12 to 15 carbons.

The composition defined in claim 3 wherein said reaction product is present in said oil at a concentration of 8 to 75 millimoles per kilogram of calcium present in said reaction product.

The composition defined in claim 3 wherein 2.5 to 10 weight percent of a polyisobutenyl succinimide of an alkylene polyamine lubricating oil detergent is also present within said oil.

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DANIEL E. WYMAN, Primary Examiner
W. H. CANNON, Assistant Examiner

U.S. Cl. X.R.

260—570.5 P, 570.9