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LUBRICATING OIL COMPOSITION

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10 Claims. (Cl. 252—32.7)

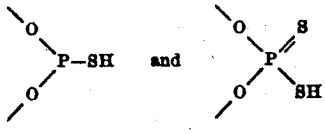
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The present invention relates to the improvement of hydrocarbon products derived from petroleum sources and more particularly to the preparation of improved lubricating oil compositions, also to a new class of additives which impart improved properties to such hydrocarbon products.

In the development of petroleum lubricating oils the trend has been to use more and more efficient refining methods in order to reduce the tendency of the oils to form carbon and deposits of solid matter or sludge. While such highly refined oils possess many advantages, their resistance to oxidation, particularly under conditions of severe service, is generally decreased and they are more prone to form soluble acidic oxidation products which are corrosive. They are generally less effective than the untreated oils in protecting the metal surfaces which they contact against rusting and corrosion due to oxygen and moisture. They also often deposit thick films of "varnish" on hot metal surfaces, such as the pistons of internal combustion engines.

In accordance with the present invention a new class of compounds has been discovered which when added to refined lubricating oils in small proportions substantially reduce the tendency of such lubricating oils to corrode metal surfaces, and they are particularly effective in inhibiting the corrosion of copper-lead and cadmium-silver bearings. These substances are also effective in dispersing sludge and in maintaining a clean engine condition. These materials are likewise effective in inhibiting oxidation of other petroleum hydrocarbon products, as will be explained more fully hereinafter.

The new class of materials which have been found to possess the stabilizing and detergent qualities above described may be defined as the oil-soluble metal salts of an aromatic methylene alkyl thioether containing a radical of a thio acid of phosphorus linked to an aromatic nucleus, said acid radical being selected from the group consisting of



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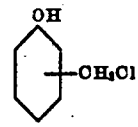
Since these radicals are divalent, one such radical will be linked to a pair of aromatic nuclei. A product of this type is conveniently formed by reacting a hydroxyaromatic compound, e. g., a phenol, with formaldehyde or trioxymethylene in the presence of hydrogen chloride to form a chlormethyl derivative of the phenol, further reacting this derivative with an alkyl mercaptan or sodium alkyl mercaptide, then further reacting the thioether product thus formed with a sulfide of phosphorus to replace the hydroxyl radical with a radical of a thio acid of phosphorus, and finally neutralizing this thio acid radical with a basic metallic substance. Alternatively, instead of preparing the chlormethyl derivative of the phenol, a hydroxymethyl derivative may be formed by reacting the phenol with formaldehyde in the presence of an alkali, and this intermediate may then be reacted with a mercaptan, preferably in the presence of an acid catalyst, and further treated as in the case of the chlormethyl derivative.

The thiophosphorous and thiophosphoric acid derivatives described above, before neutralization with a base, are effective antioxidants and stabilizing agents when incorporated in lubricating oils and other hydrocarbon materials. This invention includes the preparation and use of such unneutralized products.

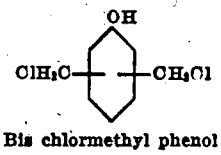
The aromatic material which may be employed may be phenol itself, an alkylated phenol, or other aromatic compound containing a hydroxyl group, e. g., a naphthol. A particularly suitable material is tertiary-octyl phenol, formed by alkylating phenol with diisobutylene. Phenols extracted from petroleum oils may be used as obtained or after alkylation. Also, naturally occurring phenols such as those found in vegetable oils, e. g., "Cardanol," which is derived from cashew nut shell oil, may be used. It is preferable to use phenols containing alkyl groups, as these impart oil solubility to the final product. However, where the product contains alkyl radicals of sufficient length from other sources, a non-alkylated phenol or like compound may be employed.

When a phenol is reacted with formaldehyde and hydrogen chloride to form a chlormethyl derivative, the product will generally consist of a mixture of related products, all containing the

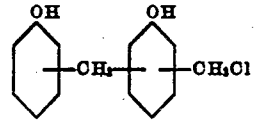
chlormethyl group. It is believed that the product consists chiefly of the following compounds:



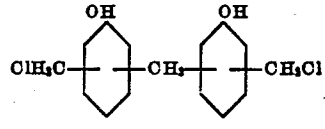
Chlormethyl phenol



Bis chlormethyl phenol



Chlormethyl bis (hydroxyphenyl) methane

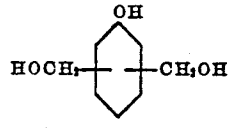


Bis (Chlormethyl hydroxyphenyl) methane

When the above mixture is reacted with a mercaptan or mercaptide, the chlorine atoms of all these compounds will be replaced by the thioalkyl group, and when this product is further reacted with a sulfide of phosphorus, the hydroxyl group of each compound will be replaced by a thiophosphite or thiophosphate radical.

If this material is finally neutralized with a metallic compound, that is, a metal containing base, the product will consist of a mixture of salts, in which the hydrogen of the sulfhydryl group of each compound is replaced by metal.

When the additive is prepared by first forming a hydroxy-methyl phenol instead of a chlormethyl phenol, it is believed that this intermediate consists substantially of the single product



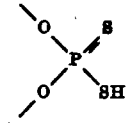
Di(hydroxymethyl phenol

and accordingly the final acid or salt product will have a similar simple composition.

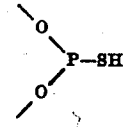
When the first formed intermediate derived from phenol, whether it is a chlormethyl derivative or a hydroxymethyl derivative, is further reacted with a mercaptan or alkali methyl mercaptide, a thioether is formed by replacing the chlorine atom or the hydroxyl group of the methylene group with an —SR group, where R is any alkyl radical, whether primary, secondary or tertiary. A particularly valuable reactant for this step of the process is tertiary-octyl mercaptan, which may be prepared by reacting diisobutylene with hydrogen sulfide in the presence of a catalyst such as boron trifluoride, for example, by the method of Example 2 of the Eby U. S. Patent 2,382,700.

After the thioether compound is formed, containing a hydroxyl group attached to an aromatic nucleus, this product is reacted with a sulfide of

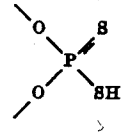
phosphorus, preferably with phosphorus pentasulfide (P_2S_5), or phosphorus heptasulfide (P_4S_7). When the reactant is phosphorus pentasulfide, the reaction results in the replacement of two hydroxyl groups with a dithiophosphoric acid radical



When phosphorus heptasulfide is used, the reaction product consists essentially of three parts of material containing a monothiophosphorous acid radical



and one part of material containing the dithiophosphoric acid radical



The additives of the present invention are preferably blended in mineral lubricating oils in the proportion of about 0.1% to about 2.0% by weight, although it will be understood that somewhat different proportions may be employed in special cases.

The following examples illustrate the preparation and testing of typical lubricating oil additives in accordance with the present invention, but it is to be understood that these examples are not to be construed as limiting the scope of the invention in any way. For convenient shipping and storage of the additives prior to incorporation in the lubricating oil base, it is desirable to prepare concentrates containing 25% to 50% of the compounds.

Example 1

To prepare the di(hydroxymethyl) tertiary-octyl phenol, a large Erlenmeyer flask was charged with the following: 1236 gms. (6 mols) p-tertiary-octyl phenol, 250 gms. sodium hydroxide dissolved in 2000 cc. of water, 800 cc. methanol, and 1314 gms. (13.1 mols) formalin. The mixture was then allowed to stand for three days at room temperature, whereupon it was neutralized with a slight excess of hydrochloric acid. (Congo red used as an indicator). The excess acid was in turn removed by neutralizing with a slight excess of sodium bicarbonate. The mixture was then extracted with ether. The extract was washed once with water and finally dried over sodium sulfate. On removal of the ether under reduced pressure at 70° C., the reaction product was obtained as a residue consisting of 1360 gms. of a light colored viscous oil which solidified on cooling. The product gave the following analytical data:

Found, C=72.16; H=9.96.
$C_{16}H_{26}O_3$ calculated, C=72.18; H=9.77.

A little of the reaction product was recrystallized from a mixture of benzol and petroleum ether.

In this state of purity the product melted at 72.0–72.5° C.

The di-(amylthiomethyl) tert.-octyl phenol was prepared from the corresponding di(hydroxymethyl) tert.-octyl phenol in the following manner:

A 3-way flask, equipped with a stirrer and a thermometer attached through a water trap, was charged with 266 gms. (1 mol) of di(hydroxymethyl) tert.-octyl phenol, 300 gms. (3 mols) of mixed amyl mercaptans, 400 cc. of xylene, and 3 gms. of toluene sulfonic acid monohydrate. The mixture was then refluxed with rapid stirring until no more water was given off, as could be seen from the level of the water in the water trap. 35 cc. of water was collected. The reaction mixture was then cooled and filtered to remove a trace of insoluble material. On removal of the solvent (100° C. and 3 mm. pressure), 326 gms. of a light colored fluid oil was obtained. This oil is designated as product A. Analysis:

Found, S=16.99.
Calculated, S=14.61.

A round bottom flask equiped with a return condenser was charged with 117.2 gms. (0.4 mol) of product A, 400 cc. dioxane and 22.2 gms. (0.1 mol) of phosphorus pentasulfide. The mixture was then refluxed until no more hydrogen sulfide was given off (5 hours). On removal of the solvent under reduced pressure, 202 gms. of red oily residue were obtained. This may be designated as product B.

Product B was dissolved in ether and placed in a large beaker; water was added, and then while stirring with a mechanical stirrer a slight excess of calcium hydroxide was added. The mixture was stirred until the aqueous layer became permanently alkaline to litmus. The ether layer was then separated from the water layer, dried over calcium chloride, and finally filtered. The filtrate was evaporated to dryness at 100° C. and 3 mm. pressure. The calcium salt was obtained as a red viscous oil, readily soluble in mineral oils. Analysis:

Found, Ca=2.92%; S=16.57; P=2.77.
Calculated, Ca=2.02%; S=19.41; P=3.13.

Example 2

To prepare the chlormethyl derivative of tert.-octyl phenol, a 3-way flask equipped with a stirrer, a return condenser and an inlet tube for hydrogen chloride, was charged with 300 gms. of trioxymethylene (10 mols) and 900 cc. of benzol. Hydrogen chloride was then passed through the mixture at room temperature with rapid stirring until 200 gms. of hydrogen chloride had been absorbed. The product was then cooled to 0° C., whereupon 824 gms. of tert.-octyl phenol (prepared by alkylating phenol with diisobutylene) was added as rapidly as possible. The temperature rose to 40° C. during the addition of the phenol.

When the reaction subsided, the mixture was heated to 45° C. with stirring and maintained at 45° to 50° C. for 3 hours. Throughout this time hydrogen chloride was bubbled through the solution to insure saturation. The product was then decanted from a small amount of unreacted trioxymethylene into ice and water, and the mixture was extracted with ether. The extract was washed several times with cold water whereupon it was dried over sodium sulfate. On removal of the ether at 70° C. under 3 mm. pressure, 935 gms. of a reaction product was obtained which consisted of a light colored viscous oil. The product contained 13.6% chlorine, which is a close approximation to the 14.02% chlorine calculated for mono-chlormethyl tert.-octyl phenol. The product, however, undoubtedly consisted of a mixture of isomers and partial condensation products, though the monomer may have predominated. This reaction product is designated as product A.

To prepare the tert.-octyl thiomethyl derivative, the following procedure was used:

A 3-way flask equipped with a stirrer, a return condenser, and a dropping funnel was charged with 900 cc. of absolute alcohol. To this was then slowly added 40.3 gms. (1.75 mol) of metallic sodium with rapid stirring and sufficient cooling to control the reaction. Finally, 256 gms. (1.75 mol) of tertiary-octyl mercaptan was added and the mixture was stirred and heated until all the sodium had dissolved. The dropping funnel was charged with 450 gms. (1.75 mol) of chlormethyl-tert.-octyl phenol (product A) dissolved in 400 cc. of absolute alcohol. This solution was then added to the reactor slowly with rapid stirring over a period of about half an hour, whereupon the mixture was refluxed for about three hours. Finally the reaction product was poured into water, acidified and extracted with ether. The extract was washed and then dried over sodium sulfate. The solvent and unreacted mercaptan were finally removed at 100° C. under 2 mm. pressure. The residue consisted of 502 gms. of a light colored soft resin, and is designated as product B.

A 3-way flask equipped with a stirrer and a return condenser was charged with 87.36 gms. (0.24 mol) of tert.-octyl thiomethyl tert.-octyl phenol (product B), and 300 cc. of dioxane. To this was then added 10.44 gms. (0.03 mol) of phosphorus heptasulfide (P_4S_7), whereupon the mixture was refluxed for 5 hours. On cooling, the reaction product was filtered to remove a trace of undissolved material. Finally, the solvent was removed at 100° C. under 2 mm. pressure. The residue consisted of 96.9 gms. of a straw-colored soft sticky resin. This product is designated as product C.

The calcium salt of the tert.-octyl thiomethyl tert.-octyl phenol-P_4S_7 condensate was prepared as follows:

4 gms. of metallic calcium was added slowly to 100 cc. of absolute ethyl alcohol to which a small crystal of mercuric chloride had been added previously to act as a catalyst. The mixture was refluxed with stirring until practically all the calcium had dissolved. The calcium ethylate thus prepared was then treated with 92.3 gms. (0.082 mol) of product C dissolved in 150 cc. of benzol. The latter reactant was added to the former over a period of 20 minutes. The mixture was then refluxed for 2½ hours, whereupon it was filtered to remove a trace of undissolved material. The filtrate was evaporated to dryness at 100° C. under 2 mm. pressure. The residue consisted of 75.8 grams of amber-colored brittle solid, which proved to be readily soluble in lubricating oils.

Example 3.—Bearing corrosion tests

Blends of the metallic salts of Examples 1 and 2 in a lubricating oil base were submitted to a corrosion test designed to measure the effectiveness of the products in inhibiting the corrosive-

ness of a typical mineral lubricating oil toward the surfaces of copper-lead bearings. The base oil employed was a paraffinic type mineral lubricating oil of SAE 20 grade. The test was applied to the unblended base oils as well as to the blends. The test was conducted as follows: 500 cc. of the oil was placed in a glass oxidation tube (13 inches long and 2⅝ inches in diameter) fitted at the bottom with a ¼ inch air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heating bath so that the oil temperature was maintained at 325° F. during the test. Two quarter sections of automotive bearings of copper-lead alloy of known weight having a total area of 25 sq. cm. were attached to opposite sides of a stainless steel rod which was then immersed in the test oil and rotated at 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. At the end of each 4-hour period the bearings were removed, washed with naphtha and weighed to determine the amount of loss by corrosion. The bearings were then repolished (to increase the severity of the test), reweighed, and then subjected to the test for additional 4-hour periods in like manner. The results are given in the following table as "corrosion life," which indicates the number of hours required for the bearings to lose 100 mg. in weight, determined by interpolation of the data obtained in the various periods.

Oil Blend	Bearing Corrosion Life (Hrs.)
Base Oil	6
Base Oil + 1% Product of Example 1	72
Base Oil + 0.5% Product of Example 2	34

Example 4.—Carbon black dispersion tests

A carbon black dispersion test was carried out, as described in U. S. Patent 2,390,342, to measure the comparative effectiveness of the additives of the present invention as agents for dispersing sludge in lubricating oil. In this test 6% by weight of activated carbon was added to the oil blend containing the additive and thoroughly dispersed in the oil by stirring with an "egg beater" type mixer for 15 minutes while the temperature of the oil was maintained at 250° F. 250 cc. of the blend was then placed in a 250 cc. graduated cylinder and allowed to settle for 24 hours while the temperature was maintained at 200° F. If an additive is not a dispersing agent, the carbon black settles rapidly at this point leaving clear oil at the top in an hour or two. A very effective disperser will maintain the carbon black in suspension so that no change in the opaque slurry is apparent even after a 24-hour period. With all but the most potent dispersing agents stratification occurs with a black layer at the bottom (high concentration of carbon black) and a blue opaque layer at the top (reduced carbon black concentration). Cases of this type, known as "blue line" separations, are only detectable in reflected light. The base oil used for this test was a paraffinic oil of SAE 20 grade. The results of the test when applied to blends containing the products of Examples 1 and 2 are shown in the following table, in which the results are shown as the volume of dispersed carbon black remaining after the settling period.

Additive Concentration	Cc. Dispersed Carbon Black
0 (Unblended Base Oil)	87 clear.
1% Product of Example 1	188 blue line.
0 (Unblended base oil)	126 clear.
0.5% Product of Example 2	250.

The products of the present invention may be employed not only in ordinary hydrocarbon lubricating oils but also in the "heavy duty" type of lubricating oils which have been compounded with such detergent type additives as metal soaps, metal petroleum sulfonates, metal phenol sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, thiophosphates, phosphites and thiophosphites, metal salicylates, metal xanthates and thioxanthates, metal thiocarbamates, amines and amine derivatives, reaction products of metal phenates and sulfur or of metal salts of phenol sulfides and sulfur, reaction products of metal phenates and phosphorus sulfides or of metal salts of phenol sulfides and phosphorus sulfides, metal phenol sulfonates, and the like. Thus, the organo-substituted acids of phosphorus and salts of the present invention may be used in lubricating oils containing such addition agents as barium tert.-octyl phenol sulfide, calcium tert.-amyl phenol sulfide, nickel oleate, barium octadecylate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum naphthenate, calcium cetyl phosphate, barium di-tert.-amyl phenol sulfide, calcium petroleum sulfonate, zinc methyl cyclohexyl thiophosphate, calcium dichlorostearate, etc.

The lubricating oil base stocks used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichlorodiethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additive present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases

auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubricating of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of Diesel engine and other gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organometallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assistant agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed.

Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol ($C_8H_{17}OH$), lauryl alcohol ($C_{12}H_{25}OH$), cetyl alcohol ($C_{16}H_{33}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol ($C_{18}H_{37}OH$), heptadecyl alcohol ($C_{17}H_{35}OH$), and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes, the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc.

In addition to being employed in crankcase lubricants the additives of the present invention may also be used in extreme pressure lubricants, engine flushing oils, industrial oils, general machinery oils, process oils, rust preventive compositions and greases.

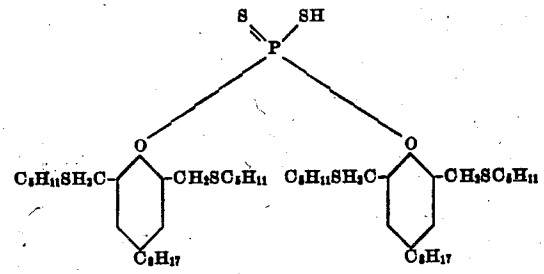
The antioxidant or stabilizing additives of the present invention may be employed not only in mineral lubricating oils, but also in hydrocarbon products generally, where improved resistance to oxidation is desired. Thus, the products may be added to motor oils, Diesel fuels, kerosene, waxes, hydrocarbon polymers, natural and synthetic rubbers, etc.

The present invention is not to be considered as limited by any of the examples described herein, which are given by way of illustration only,

but is to be limited solely by the terms of the appended claims.

I claim:

1. A lubricating composition comprising a mineral lubricating oil base and an oxidation inhibiting amount of a member of the group consisting of a compound of the structure

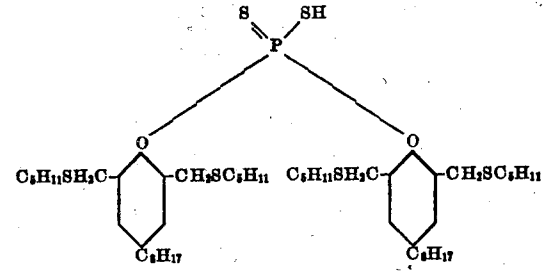


and alkaline earth metal salts thereof.

2. A lubricating oil composition in accordance with claim 1 in which the additive is a salt of calcium.

3. A lubricating composition comprising a mineral lubricating oil base and an oxidation inhibiting amount of a material consisting of approximately 3 molecular proportions of a calcium salt of the monothiophosphorous acid derivative of the tertiary-octyl phenol methylene tertiary-octyl thioether and about 3 molecular proportions of a calcium salt of the dithiophosphoric acid derivative of the tertiary-octyl phenol methylene tertiary-octyl thioether.

4. As a new composition of matter an alkaline earth metal salt of a compound of the structure



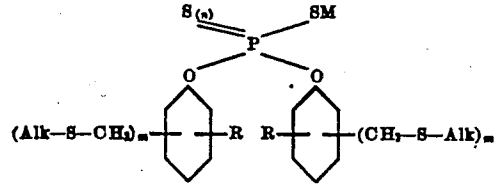
5. As a new composition of matter a mixture of about three molecular proportions of a calcium salt of the mono-thiophosphorous acid derivative of the tertiary-octyl phenol methylene tertiary-octyl thioether and about one molecular proportion of a calcium salt of the dithiophosphoric acid derivative of the tertiary-octyl phenol methylene tertiary-octyl thioether.

6. The process of preparing a calcium salt of an aromatic methylene thioether which comprises reacting tertiary octyl phenol with trioxymethylene in the presence of hydrogen chloride to form a chlormethyl derivative, reacting such chlormethyl derivative with sodium tertiary octyl mercaptide in sufficient quantity to convert the chlormethyl derivative into a thioether, further reacting the product thus formed with phosphorus heptasulfide to replace the hydroxyl groups with radicals of thio acids of phosphorus, and reacting the product last formed with calcium ethylate.

7. The process of preparing a calcium salt of an aromatic methylene thioether compound which comprises reacting tert.-octylphenol with formaldehyde in the presence of methanol and sodium hydroxide, followed by neutralization of the alkaline mixture with an acid, whereby di-(hydroxymethyl) tert.-octylphenol is formed, further reacting this product with amyl mer-

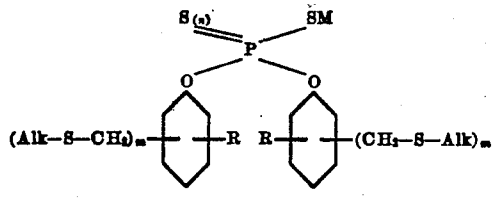
captan to convert the former into di(amyl thiomethyl) tert.-octylphenol, further reacting the latter with phosphorus pentasulfide to form a dithiophosphoric acid, and finally neutralizing such acid with calcium hydroxide.

8. A lubricating composition comprising a mineral lubricating oil base and an oxidation inhibiting amount of a compound of the structure



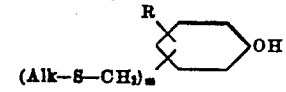
wherein M represents an alkaline earth metal, m is a number from 1 to 2, n is a number from 0 to 1, R is selected from the group consisting of hydrogen and alkyl radicals, and "Alk" is an alkyl radical.

9. As a new composition of matter a compound of the structure



wherein M represents an alkaline earth metal, m is a number from 1 to 2, n is a number from 0 to 1, R is selected from the group consisting of hydrogen and alkyl radicals, and "Alk" is an alkyl radical.

10. The process of preparing an aromatic methylene thioether compound which comprises reacting a compound of the formula



where R is selected from the group consisting of hydrogen and alkyl radicals, "Alk" is an alkyl radical, and m is a number from 1 to 2, with a sulfide of phosphorus.

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