

UNITED STATES PATENT OFFICE

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LUBRICATING OIL

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9 Claims. (Cl. 260—461)

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This invention relates to a mineral lubricating oil and more particularly to a new type of additive which imparts pour stabilizing properties to such oil and improves other properties of the same.

This application is a continuation-in-part of my copending application Serial No. 653,152, filed March 8, 1946, (now Patent No. 2,443,264) which is a division of application Serial No. 523,091, filed February 19, 1944 (now abandoned).

In accordance with the present invention a new class or organic compositions are described which are useful as additives for mineral lubricating oils, particularly those which are used in internal combustion engines, in which they act as pour depressing and pour stabilizing agents, also as inhibitors of oxidation.

The new class of additives have been found not only to be effective in substantially reducing the ASTM pour point of a lubricating oil, but in stabilizing the pour point, thus providing a stable lubricating oil which will not solidify under conditions of fluctuating temperature involved in normal outdoor conditions. The new additives of the present invention have been submitted to tests which simulate the normal varying temperature conditions encountered in winter field service, and satisfactory results were obtained from their use, as will be explained more particularly hereinafter.

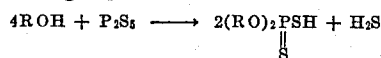
In serving as inhibitors of oil deterioration, the new additives aid in the prevention of ring sticking, piston skirt varnish formation, deposition of sludge, and the like. They are particularly useful in inhibiting the normal corrosiveness of the oil when in contact with copper-lead, cadmium-silver and other similar bearings, now widely used in automotive engines.

The new class of compounds which are employed as additives in accordance with the present invention are organic compounds containing both phosphorus and sulfur and may be considered as polysulfide derivatives of thiophosphoric and thiophosphorous acids, the latter being obtained by reacting a sulfide of phosphorus with a mixture of a wax-phenol and an aliphatic alcohol. It has been found that the reaction product derived from a mixture of a wax-phenol and an alcohol is superior to similar products derived from wax-phenol or other alkylated phenols alone in possessing superior oil solubility. It is believed that the presence of the alcohol prevents the formation of products of too high molecular weight.

When the mixture of wax-phenol and alcohol is reacted with phosphorus pentasulfide, it is be-

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lieved that the reaction proceeds according to the following equation:



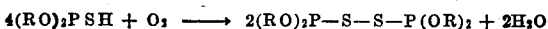
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In the above equation R represents the wax-phenol radical and/or the aliphatic radical from the alcohol, the equation representing a statistical average of reactions among the various molecules. Undoubtedly in many cases the thiophosphoric acid molecule will contain both the wax-phenol and the aliphatic radicals.

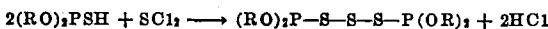
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In forming the polysulfide derivatives of such thiophosphoric acid or thiophosphorous acid, the acid is treated with an oxidizing agent, e. g., iodine, potassium triiodide, ferric chloride, sodium hypochlorite, or oxygen itself, or with sulfur dichloride or sulfur monochloride, to form a disulfide, trisulfide or tetrasulfide, respectively, according to the following equations:

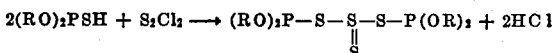
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The wax-phenols employed in accordance with the present invention may be derived in the usual manner by first chlorinating paraffin wax and then reacting the latter with phenol. The aliphatic alcohols which are employed in conjunction with such phenols may be any aliphatic alcohols, particularly suitable examples being methyl alcohol, ethyl alcohol, isopropyl alcohol, octyl alcohol, decyl alcohol, stearyl alcohol, oleyl alcohol, and the like. The mixture of wax-phenol and alcohol may be reacted with any of the sulfides of phosphorus, such as P_2S_3 , P_2S_5 , P_4S_3 , P_4S_7 , and the like.

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The ratio of alcohol to phenol may be varied within wide limits. The higher the molecular weight of the wax phenol, the higher the ratio has to be in order to obtain satisfactory oil solubility. Generally, a preferred ratio is one to two wax-phenol hydroxyl groups to one molecule of alcohol.

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In employing the additives of the present invention for use either as pour depressants or as corrosion inhibitors, it has been found desirable to use the same in the proportions of about 0.02% to 3%, preferably about 0.1% to 2%, based on the lubricating oil base stock.

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In the following examples are illustrated methods for the preparation of typical products of the present invention, and tests of the same

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illustrating their usefulness when compounded with mineral lubricating oils. It is to be understood that these examples are illustrative only and are not to be considered as limiting the scope of the invention in any way.

Example 1.—Preparation of substituted thiophosphoric acid

A three-way flask equipped with a stirrer and return condenser was charged with 51 g. of wax-phenol (prepared by heating 450 g. of chloroparaffin containing 14% Cl with 90 g. phenol in the presence of AlCl_3), 15.8 g. decanol (decyl alcohol), 22.2 g. P_2S_5 , and 150 cc. dioxane. (The amounts of wax-phenol and decanol were calculated to provide 2 wax-phenol hydroxyl groups for each molecule of decanol.) The mixture was refluxed until no more H_2S was given off (about $2\frac{1}{2}$ hours). The reaction product was then dissolved in ether and transferred into a large beaker containing a volume of water approximately equal to the volume of the ether solution. Then while the mixture was rapidly stirred, a slight excess of hydrated lime was added. The mixture was stirred until the aqueous solution remained permanently alkaline to litmus. The ether layer was then separated from the aqueous layer and the extract was dried over calcium chloride. The ether was removed on a steam bath and the residue was taken up with acetone. The small amount of undissolved material was filtered off and the acetone was removed at 100°C . under 2 mm. pressure. The product was obtained as a soft resin readily soluble in lubricating oils.

Example 2.—Preparation of the disulfide derivative

A portion of the substituted thiophosphoric acid produced as described in Example 1 was suspended in water and treated with an aqueous solution of potassium triiodide with vigorous shaking. When no more iodine was being absorbed, as could be seen from the brown color imparted to the aqueous layer, the addition of the potassium triiodide was discontinued. Finally the reaction mixture was decolorized with sodium bisulfite solution. The reaction product was then extracted with ether, washed with dilute sodium hydroxide solution and finally dried over sodium sulfate. On removal of the ether, a viscous reddish brown residue was obtained which was found to be readily soluble in lubricating oils.

Example 3.—Preparation of the trisulfide derivative

A portion of the substituted thiophosphoric acid obtained in the preparation of Example 1 was dissolved in an equal volume of dioxane and was treated with SCl_2 in the ratio of one mol of SCl_2 to 2 mols of the acid. The mixture was then heated at 80°C . for about 2 hours, whereupon it was poured into water and extracted with ether. The ether extract was then dried over sodium sulfate. On removal of the ether the reaction product was obtained as a viscous brown oil, readily soluble in mineral oils.

Example 4.—Pour point and pour stability tests

In these tests the ASTM pour point and the solid point as determined by the pour stability test described below were measured, using various concentrations of disulfide and trisulfide products of Examples 2 and 3 in a waxy base mineral lubricating oil consisting of an acid-

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treated Mid-Continent neutral oil with the addition of $3\frac{1}{2}\%$ of Pennsylvania bright stock, this oil having a viscosity of SAE 10 grade and a cloud point of $+34^\circ\text{F}$.

The pour stability of the various oil blends containing the new additives was determined by a test in which the temperature was varied to simulate rather severe winter temperature conditions. More specifically, the samples were first gradually reduced in temperature from room temperature to $+15^\circ\text{F}$. during the first day of the test, then warmed gradually to $45-50^\circ\text{F}$. during the second day, then held at about 35°F . for two days, these temperatures being close to the cloud points of the oil samples, and finally the temperature was gradually lowered to -20° to -25°F . during the last 24 hours. The temperature at which the oil samples became solid under these conditions was taken as the "solid point." The results obtained with the tests applied to the unblended base oil and to the same when blended with various concentrations of the original wax-phenols and with the products of Examples 2 and 3 are shown in the following table:

Oil Blend	Additive Concentration	ASTM Pour Point, $^\circ\text{F}$.	Pour Stability (Solid Point), $^\circ\text{F}$.
Base Oil.....		$+30$	$+15$
Base Oil+Wax-phenol.....	0.25	-20	$+15$
	0.50	-30	
	1.00	-35	
Base Oil+Product of Ex. 2.....	0.25	-25	-5
	0.50	-20	
	1.00	-40	
Base Oil+Product of Ex. 3.....	0.25	0	-22
	0.50	-20	
	1.00	-30	

It can be seen from the above data that although the wax-phenols themselves possess good pour reducing properties, the pour stability of the blend containing the same is very poor; while the disulfide and trisulfide products of Examples 2 and 3 exhibit good pour stabilizing properties as well as excellent pour depressing properties.

Example 5.—Bearing corrosion test

A test was made of the effect of the disulfide product of Example 2 in reducing the corrosiveness of a lubricating oil toward a copper-lead bearing, using a blend containing 1% of the additive in a solvent extracted Mid-Continent paraffinic lubricating oil of SAE 30 viscosity grade. A similar test was made of the unblended base. The test was conducted as follows: 500 cc. of the oil was placed in a glass oxidation tube (13 inches long and $2\frac{3}{8}$ inches in diameter) fitted at the bottom with a $\frac{1}{4}$ 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 "corro-

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sion 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	Bearing Corrosion Life, Hours
Base Oil.....	4
Base Oil+1% Product of Ex. 2.....	20

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 additive as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, thiophosphates, phosphites and thiophosphites, metal salicylates, metal xanthates and thioxanthates, metal thio-carbamates, amines and amine derivatives, reaction products of metal phenates and sulfur, reaction products of metal phenates and phosphorus sulfides, metal phenol sulfonates, and the like. Thus, the polysulfide derivatives of the organo-substituted thio acids of phosphorus 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, dichlorodimethyl 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, either alone or in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additives 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 aux-

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iliary 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 service, particularly with high speed Diesel engines, and in aviation 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, organo metallic 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 assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed.

Assisting agents which are particularly desirable 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 present invention is not to be considered as limited by any of the samples herein which are given by way of illustration only, but it is to be limited solely by the terms of the appended claims.

I claim:

1. As a new composition of matter the product obtained by reacting a mixture of substantially equal molecular proportions of paraffin wax-phenol and decanol with a sufficient amount of phos-

phorus pentasulfide to convert the wax-phenol and decanol into dithiophosphoric acids and further reacting the product thus formed with potassium triiodide.

2. As a new composition of matter the product obtained by reacting a mixture of substantially equal molecular proportions of paraffin wax-phenol and decanol with a sufficient amount of phosphorus pentasulfide to convert the wax-phenol and decanol into dithiophosphoric acids and further reacting the product thus formed with sulfur dichloride.

3. As a new composition of matter the product obtained by reacting a mixture of substantially equal molecular proportions of paraffin wax-phenol and decanol with a sufficient amount of phosphorus pentasulfide to convert the wax-phenol and decanol into dithiophosphoric acids and further reacting the product thus formed with sulfur monochloride.

4. As a new composition of matter the product obtained by reacting a mixture of paraffin wax-phenol and an unsubstituted aliphatic monohydroxy alcohol containing 1 to 18 carbon atoms per molecule, such mixture having 1 to 2 wax-phenol hydroxyl groups for each molecule of alcohol, with a sufficient amount of phosphorus pentasulfide to convert the phenol and alcohol present into dithiophosphoric acids, and further converting the product thus formed with an oxidizing agent selected from the group which consists of potassium triiodide, sulfur dichloride, and sulfur monochloride capable of converting the same into a polysulfide.

5. As a new composition of matter the product obtained by (1) forming a wax-phenol by condensing one molecular proportion of chlorinated paraffin wax containing 14% chlorine with about one molecular proportion of phenol, (2) mixing the wax-phenol thus formed with decanol in proportions that will provide about two phenol hydroxyl groups for each molecule of decanol, (3) reacting the mixture thus formed with a sufficient amount of phosphorus pentasulfide to convert the same into dithiophosphoric acids, and (4) reacting the acids thus formed with a sufficient amount of sulfur dichloride to convert the same into a trisulfide derivative.

6. A method of preparing an oil soluble additive for mineral lubricating oils which comprises reacting a mixture of paraffin wax-phenol and an unsubstituted aliphatic monohydroxy alcohol containing 1 to 18 carbon atoms, such mixture

having 1 to 2 wax-phenol hydroxyl groups for each molecule of alcohol, with a sufficient amount of phosphorus pentasulfide to convert the phenol and alcohol present into dithiophosphoric acids, and further converting the product thus formed with an oxidizing agent selected from the group which consists of potassium triiodide, sulfur dichloride, and sulfur monochloride capable of converting the same into a polysulfide.

7. A method according to claim 6 in which the aliphatic alcohol is decanol and in which the dithiophosphoric acids are converted into a disulfide product.

8. A method according to claim 6 in which the aliphatic alcohol is decanol and in which the dithiophosphoric acids are converted into a trisulfide product.

9. A method of preparing an oil soluble additive for mineral lubricating oils which comprises (1) forming a wax-phenol by condensing about one molecular proportion of chlorinated paraffin wax containing 14% chlorine with about one molecular proportion of phenol, (2) mixing the wax-phenol thus formed with decanol in proportions which will provide about two wax-phenol hydroxyl groups for each molecule of decanol, (3) reacting the mixture thus formed in dioxane solution with phosphorus pentasulfide in sufficient amount to convert the wax-phenol and decanol into dithiophosphoric acids at the refluxing temperature of the mixture, and (4) reacting the dithiophosphoric acids formed in the previous step with a sufficient amount of sulfur dichloride to convert the said acids into a trisulfide derivative, the reaction being conducted in dioxane solution at about 80° C.

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