Patented Sept. 14, 1954

2,689,258

UNITED STATES PATENT OFFICE

2,689,258

REACTION OF TERPENES WITH THIOPHOSPHOROUS ACID ESTERS AND PRODUCTS THEREOF

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No Drawing. Application April 21, 1948, Serial No. 22,513

6 Claims. (Cl. 260—461)

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The present invention relates to new compounds having oxidation inhibiting properties and more particularly to the use of such compounds as oxidation inhibiting additives for hydrocarbon products.

In the development of 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 acid 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 chemical compounds has been discovered, and these compounds have been found to reduce the tendency of refined lubricating oils and other hydrocarbon products to corrode metal surfaces when added in small quantities to such materials. These additives are particularly active in reducing the corrosion of copper-lead and cadmium-silver bearings which are employed in internal combustion engines, and they are likewise effective in inhibiting the oxidation of hydrocarbon products generally and especially those of petroleum origin.

The new class of compounds forming the subject of the present invention are bornyl esters of organo-substituted thiophosphorous and thiophosphoric acids. These esters may be conveniently formed by reacting a dicyclic terpene with the organo-thiophosphorous or organo-thiophosphoric acid such as a diester of dithiophosphoric acid. The reaction is exothermic and is conveniently brought about by contacting the reacting compounds at normal atmospheric temperatures. The reactants are conveniently employed in a mol/mol ratio, but the reaction will nevertheless take place with any proportions of reactants. Where the product is to be employed as an antioxidant for hydrocarbon materials it is desirable not to have present more than one mol of acid for each mol of the terpene. Whenever either reactant is present in excess of a mol/mol ratio, which is always the ratio involved in the actual reaction, the excess merely remains as a diluent of the reaction product.

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The new class of compounds of the present invention may be more accurately defined as the bornyl esters of organo-substituted acids of phosphorus which have the general formula

$$(RX)_2\overset{S_n}{\overset{\|}{P}}—SH$$

in which R represents a hydrocarbon radical, such as an alkyl, cycloalkyl, aryl, aralkyl, or alkaryl radical, with or without certain substituents which may be sulfur, halogens or nitro groups, and such hydrocarbon radicals may also contain ether linkages; that is, an oxygen atom may be inserted at any point in the radical, thus separating the radical into two shorter hydrocarbon radicals. Expressed differently, a hydrocarbon radical may be extended by substituting an ether group for a hydrogen atom. In the above formula X represents oxygen or sulfur, and n may be 0 or 1, depending upon whether the acid is a thiophosphorous or thiophosphoric acid.

A preferred subclass of the above esters, readily prepared from commercially available materials, consists of the bornyl esters of the dialkyl dithiophosphoric acids. Such acids have the formula

$$(RO)_2\overset{S}{\overset{\|}{P}}—SH$$

where R is an alkyl radical.

The desired bornyl esters of the above defined acids may be formed by reacting the acids with any dicyclic terpene, of which pinene is a particularly preferred example. Other dicyclic terpenes are camphene and fenchene. Essential oils which contain these materials, such as oil of turpentine, may be employed in place of the pure terpene compounds.

The organo-substituted acids of phosphorus which may be employed in the preparation of the esters of the present invention may have hydrocarbon groups which are linear or cyclic, straight chain or branched chain, long or short, saturated or unsaturated, and may have substituent atoms or groups, as described above.

Since the organo-substituted thiophosphorous and thiophosphoric acids are usually prepared by reacting alcohols, mercaptans, phenols or thiophenols with sulfides of phosphorus, it is possible to use as starting materials a large variety of these compounds. For example, alcohols of the type of ethyl alcohol, isopropyl alcohol, tert.-butyl alcohol, lauryl alcohol, stearyl alcohol, wax alcohols, alcohols obtained by the oxidation of petroleum hydrocarbons, or by reaction of an olefin, carbon monoxide, and hydrogen by the

"Oxo" process, oleyl alcohol, sulfurized oleyl alcohol, chlorinated and nitrated alcohols, cyclohexyl alcohol, benzyl alcohol, alkyl mercaptans, phenol, alkylated phenols, naphthol, sulfurized phenols, thiophenols, and the like are suitable materials. Also there may be mentioned alcohols containing ether groups typified by ethylene glycol monomethyl ether, ethylene glycol monohexyl ether, propylene glycol monooctyl ether, and the like. Such compounds are conveniently prepared by reacting the alcohols with alkylene oxides. Alcohols or phenols containing aryl ether or thioether groups may similarly be employed.

The new compounds of the present invention are particularly useful as additives for mineral lubricating oils and other hydrocarbon products for the purpose of preventing corrosion of metal surfaces with which they come in contact and generally for the purpose of inhibiting oxidation and consequent deterioration of the oil. For this purpose, the amount of the additive required is generally from about 0.2 to 5% or even 10% by weight, relative to the base stock in which it is incorporated. For the purpose of storage and transportation, it is often convenient to prepare hydrocarbon oil concentrates of the additives containing from 25% to 75% by weight of the additive. When it is desired to prepare such concentrates, the esters may be conveniently prepared by reacting the terpene and acid of phosphorus in a hydrocarbon medium in concentrations sufficient to produce a concentrate of the desired strength.

The following examples illustrate the preparation of the new compounds of the present invention and the testing of certain of these compounds for their corrosion inhibiting properties when employed in lubricating oil compositions. It is to be understood, however, that these examples are not to be considered as limiting the scope of the invention in any way.

Example 1.—Bornyl ester of di-n-propyl dithiophosphoric acid

A 1-liter, 3-necked flask equipped with a stirrer, reflux condenser, and thermometer, was charged with 120 g. (2 mols) of n-propanol and 111 g. (0.5 mol) of P_2S_5. The temperature rose to 92° C. over a period of about 10 minutes. The reaction mixture was then heated at 95° C. for 25 minutes after which it was filtered to remove a small amount of unreacted P_2S_5. The di-n-propyl dithiophosphoric acid thus formed (0.86 mol) was added dropwise over a period of 1½ hours to 117 g. (0.86 mol) of pinene contained in a 4-necked, 1-liter flask equipped with a stirrer, reflux condenser, thermometer, and dropping funnel. The reaction was exothermic, the temperature rising from 25° to 38° C. The product was then heated for 1 hour at 115° C. with rapid stirring. After cooling to room temperature it was washed successively with 200 cc. of distilled water, two 200 cc. portions of 10% aqueous Na_2CO_3 solution, and 200 cc. of distilled water. The cloudy organic layer was transferred to a 1-liter beaker and blown with nitrogen for 20 minutes at 110° C., followed by filtration to remove a small amount of insoluble material. A clear, brownish red liquid was obtained, which upon analysis was found to contain 9.5% phosphorus and 16.9% sulfur.

Example 2.—Bornyl ester of diethyl dithiophosphoric acid

A 1-liter, 3-necked flask equipped with a stirrer, reflux condenser, and thermometer was charged with 276 g. (6 mols) of absolute ethanol and 333 g. (1.5 mols) of P_2S_5. The temperature rose to 70° C. within 15 minutes. After heating for an additional 20 minutes at 80° C., the product was filtered to remove a small amount of insoluble material. The diethyl dithiophosphoric acid thus formed (2.4 mols) was added to 326 g. (2.4 mols) of pinene in a 4-necked, 3-liter flask equipped with a stirrer, reflux condenser, thermometer, and dropping funnel over a period of 1½ hours, during which time the temperature rose from 25° to 36° C. The product was then heated at 115° C. for 2 hours, after which it was permitted to stand overnight. The material was then worked up in the same manner as described in Example 1. A clear reddish liquid was obtained, which upon analysis was found to contain 10.4% phosphorus and 19.3% sulfur.

Example 3.—Bornyl ester of di-(tert.-octylphenyl) dithiophosphoric acid

206 g. (1 mol) of tert.-octylphenol contained in a 3-necked, 1-liter flask equipped with a stirrer, reflux condenser, and thermometer, was heated until fluid (about 85° C.), after which 55.5 g. (0.25 mol) of P_2S_5 was added. The reaction mixture was then heated for 1 hour at 145° C., after which it was filtered to remove a small amount of unreacted P_2S_5. To 45.7 g. (0.34 mol) of pinene, contained in a 4-necked, 1-liter flask equipped with a stirrer, reflux condenser, thermometer and dropping funnel, was added 170 g. (0.34 mol) of the di-(tert.-octylphenyl) dithiophosphoric acid, formed as described above, over a period of about 1 hour, during which time the temperature rose from 30° to 48° C. The reaction mixture was then heated at 115° C. for 1 hour. A clear, pale red, very viscous liquid was obtained, which upon analysis was found to contain 4.6% phosphorus and 9.4% sulfur.

Example 4.—Bornyl ester of di-n-propyl thiophosphorous acid

A 3-necked, 1-liter flask equipped with a stirrer, reflux condenser, and thermometer, was charged with 240 g. (4 mols) of n-propanol and 174 g. (0.5 mol) of P_4S_7. The temperature rapidly rose to 52° C. After 20 minutes, the temperature was raised to 120° C. and held at this point for 2 hours. The product, after filtering to remove a small amount of P_4S_7, consisted essentially of di-n-propyl thiophosphorous acid. To 109 g. (0.8 mol) of pinene contained in a 4-necked, 1-liter flask equipped with a stirrer, reflux condenser, thermometer, and dropping funnel, was added 152 g. (0.8 mol) of the di-n-propyl thiophosphorous acid formed as described above, over a period of 1 hour, during which time the temperature rose to 45° C. After stirring for 2 hours at 105° C., the product was filtered. A clear yellow liquid was obtained, which upon analysis was found to contain 10.7% phosphorus and 13.2% sulphur.

Example 5.—Bornyl ester of di-(sulfurized oleyl) dithiophosphoric acid

A mixture of 268 g. (1 mol) of oleyl alcohol and 32 g. (1 mol) of sulfur was heated for 1 hour at 165° C. with rapid stirring in a 3-necked, 1-liter flask equipped with a stirrer, thermometer and reflux condenser. The clear dark red liquid was allowed to cool to room temperature after which 55.5 g. (0.25 mol) of P_2S_5 was added. This mixture was heated at 95° C. for 40 minutes, after which it was filtered to remove a small amount

of unreacted P_2S_5. To 54.4 g. (0.4 mol) of pinene contained in a 4-necked, 1-liter flask equipped with a stirrer, thermometer, dropping funnel and reflux condenser, was added 277.6 g. (0.4 mol) of the di-(sulfurized oleyl) dithiophosphoric acid prepared as described above, over a period of 1 hour, during which time the temperature rose from 26° to 36° C. The product was then heated at 115° C. for 1 hour with rapid stirring. A clear, viscous, dark red liquid was obtained, which upon analysis was found to contain 3.2% phosphorus and 15.1% sulfur.

Example 6.—Laboratory corrosion tests

Lubricating oil blends were prepared containing 0.25% by weight of each of the products prepared in Examples 1 to 5, using as a base oil an extracted Mid-Continent paraffinic type lubricating oil of SAE 20 grade. These blends and a sample of the unblended oil were submitted to a corrosion test designed to measure the effectiveness of the new compounds in inhibiting the corrosiveness of a typical mineral lubricating oil toward the surfaces of copper-lead bearings. 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 Composition	Bearing Corrosion Life (Hrs.)
Base Oil	9
Base Oil+0.25% bornyl ester of di-n-propyl dithiophosphoric acid (Product of Example 1)	33
Base Oil+0.25% bornyl ester of di-ethyl dithiophosphoric acid (Product of Example 2)	18
Base Oil+0.25% bornyl ester of di-(tert.-octylphenyl) dithiophosphoric acid (Product of Example 3)	28
Base Oil+0.25% bornyl ester of di-n-propyl thiophosphorous acid (Product of Example 4)	41
Base Oil+0.25% bornyl ester of di-(sulfurized oleyl) dithiophosphoric acid (Product of Example 5)	22

Example 7.—Chevrolet engine test

A blend containing 1.0% of the product of Example 1 in a solvent extracted Mid-Continent paraffinic SAE 10 oil and a sample of the unblended oil base were employed as the crankcase oil in 36-hour tests with a Chevrolet engine operated at 30 brake H. P., 3150 R. P. M. speed, 280° F. oil temperature and 200° F. jacket temperature. After each test was completed, the weight loss of the copper-lead bearing was determined. The results are shown in the following table:

Oil Composition	Bearing Wt. Loss (Gm./ Bearing)
Base Oil	2.1
Base Oil+1.0% bornyl ester of di-n-propyl dithiophosphoric acid (Product of Example 1)	1.3

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 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, reaction products of metal phenates and phosphorus sulfides, metal phenol sulfonates, and the like. Thus, the additives of the present invention may be used in lubricating oils containing such other addition agents as barium tert.-octylphenol sulfide, calcium tert.-amylphenol sulfide, nickel oleate, barium octadecylate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum naphthenate, calcium cetyl phosphate, barium di-tert.-amylphenol sulfide, calcium petroleum sulfonate, zinc methyl cyclohexyl thiophosphate, calcium dichlorostearate, etc. Other types of additives, such as phenols and phenol sulfides may be employed.

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. Hyrogenated 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. 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 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., and by the "Oxo" reaction of olefins, carbon monoxide and hydrogen.

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 additives of the present invention may be employed as antioxidant or stabilizing agents 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, and the like.

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.

What is claimed is:

1. As a new composition of matter an ester formed by reacting together a dicyclic terpene and an organo-substituted acid of phosphorus of the formula:

$(RO)_2P—SH$

where R is an alkyl hydrocarbon radical, said reaction involving about one mol of terpene to one mol of said acid of phosphorus.

2. As a new composition of matter an ester formed by reacting a pinene with a di-alkyl thiophosphorous acid with sufficient heat to complete the reaction involving about one mol of said pinene and one mol of said acid.

3. As a new composition of matter, the pinene ester of di-n-propyl thiophosphorous acid prepared by heating together pinene and said acid whereby substantially equal molar quantities of the pinene and acid react.

4. The process which comprises heating together a di-cyclic terpene and a dialkyl thiophosphorous acid whereby substantially equal molar quantities of said terpene and said acid react.

5. The process which comprises heating together pinene and a di-alkyl thiophosphorous acid whereby substantially equal molar quantities of said pinene and said acid react.

6. The process which comprises heating together pinene and di-n-propyl thiophosphorous acid whereby substantially equal molar quantities of said pinene and said acid react.

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