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PROCESS FOR REACTING DI-ORGANO SUBSTITUTED DITHIOPHOSPHORIC ACID COMPOUNDS AND EPOXIDES

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9 Claims. (Cl. 260—461)

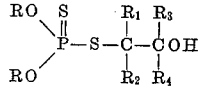
The present invention relates to the improvement of hydrocarbon products derived from petroleum sources and more particularly to the preparation of improved mineral lubricating oil compositions by the incorporation therein of a new class of additives which impart improved properties to such hydrocarbon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

This application is a division of patent application Serial No. 192,617, filed on October 27, 1950, now abandoned.

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. Although generally superior to lightly refined oils they may deposit films of "varnish" on hot metal surfaces, such as the pistons of internal combustion engines, under very severe engine operating conditions.

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 oils to corrode metal surfaces, and which are particularly effective in inhibiting the corrosion of copper-lead and cadmium-silver bearings. They are likewise effective in inhibiting oxidation of such oils and other petroleum hydrocarbon products, as will be more fully explained hereinafter.

The new class of materials which have been found to possess the antioxidant and stabilizing qualities described above are reaction products of organo-substituted dithiophosphoric acids and epoxides. Such products may be defined broadly by the formula—



where R is an aliphatic, cycloaliphatic, aromatic, aliphatic-aromatic, sulfurized aliphatic, sulfurized aromatic, or sulfurized aliphatic-aromatic hydrocarbon radical, and where R_1, R_2, R_3, and R_4 each represent hydrogen, an aliphatic hydrocarbon radical containing 1 to 4 carbon atoms, or a phenyl radical. It is to be understood that the hydrocarbon radicals represented by R in the above formula may also contain inert substituents such as halogen atoms or nitro groups.

The following typical examples are representative of the dithiophosphoric acids which may be reacted with epoxides in accordance with the present invention:

Diisopropyl dithiophosphoric acid
Di-n-butyl dithiophosphoric acid
Diisobutyl dithiophosphoric acid
Di-n-octyl dithiophosphoric acid
Di-tert.-octyl dithiophosphoric acid
Di-(ethylhexyl) dithiophosphoric acid
Dinonyl dithiophosphoric acid
Di-(C_8 oxo) dithiophosphoric acid
Dioleyl dithiophosphoric acid
Dilauryl dithiophosphoric acid
Di-(methylcyclohexyl) dithiophosphoric acid
Di-(isopropylcyclohexyl) dithiophosphoric acid
Diphenyl dithiophosphoric acid
Di-(tert.-octylphenyl) dithiophosphoric acid
Di-(2,4,6-triisobutylphenyl) dithiophosphoric acid
Di-(sulfurized oleyl) dithiophosphoric acid
Di-(tert.-octylphenol sulfide) dithiophosphoric acid

The above listed dithiophosphoric acids may be prepared by reacting an alcohol or phenol with phosphorus pentasulfide by means well known in the art, and it is to be understood that the invention applies not only to simple acids but to mixtures of acids formed by reacting phosphorus pentasulfide with mixtures of alcohols, such, for example as the mixtures of C_{10} to C_{18} aliphatic alcohols known as "Lorol" alcohols, and the mixture of alcohols derived by the oxidation of paraffin wax. Included also are products derived from the mixture of branched chain aliphatic alcohols obtained in the "oxo" process.

An important class of dithiophosphoric acids which may be employed to particular advantage and which produce reaction products of unusual potency in inhibiting corrosion comprise dithiophosphoric acids containing sulfurized organic groups. These may be sulfurized aliphatic groups, such as sulfurized oleyl radicals and similar radicals obtained by the sulfurization of unsaturated aliphatic radicals, also the sulfurized products obtained by sulfurizing phenol or alkylated phenols, otherwise known as phenol sulfides. The latter may contain one or more sulfur atoms in a linkage between two aryl nuclei.

The epoxides which may be reacted with the dithiophosphoric acids in accordance with this invention include especially the well-known alkylene oxides, such as ethylene oxide, propylene oxide, the butylene and isobutylene oxides, and a butadiene monoxide, also styrene oxide.

The reaction between the dithiophosphoric acid and the epoxide is a spontaneous exothermic reaction which takes place immediately upon contact of the reactants at normal room temperatures, and may be conveniently conducted by adding the epoxide slowly while rapidly stirring the reaction mixture and controlling the temperature by means of a water or ice bath. No catalyst is required, and the time required for the completion of the reaction is not greater than two hours and is usually much less. Solvents are not normally required, but in some cases it may be convenient to conduct the reaction in the presence of well known inert solvents such as ethylene dichloride, benzene, xylene, or a mineral oil.

The amount of the additives of the present invention which is to be employed in mineral lubricating oil compositions or other petroleum hydrocarbon compositions will normally range from about 0.02% to 5%, more generally from about 0.1 to about 2%, and the particular amount in individual cases will be selected in accordance with the requirements of the case and in view of the properties of the base stock employed. For commercial purposes, it is convenient to prepare concentrated oil solutions in which the amount of additive in the composition ranges from 25 to 50% by weight, and to transport and store them in such form. In preparing a lubricating oil composition for use as a crankcase lubricant the additive

concentrate is merely blended with the base oil in the required amount.

The preparation and testing of the additives of the present invention are illustrated in the examples described below, but it is to be understood that the additives prepared and their application in various tests are illustrative only and are not to be construed as limiting the scope of the invention in any manner.

Example 1.—Di(C_8oxo) dithiophosphoric acid-propylene oxide reaction product

A C_8 oxo alcohol was prepared by reacting CO and H_2 with a C_7 olefin fraction obtained by polymerizing a mixed propylene-butylene feedstock and hydrogenating the resulting aldehyde. The di-(C_8 oxo) dithiophosphoric acid was prepared by heating a mixture of 260 g. (2 mols) of the C_8 oxo alcohol, 111 g. (0.5 mol) of P_2S_5, and 354 g. of a light mineral oil in a 3-necked 2-l. flask equipped with a stirrer, thermometer, and reflux condenser, for 1 hour at 110° C. After filtration, the product (an approximately 50% oil solution of di-(C_8 oxo) dithiophosphoric acid) was blown with nitrogen for 30 minutes on the steam bath to remove H_2S.

The oil-acid solution was placed in a 4-necked 2-l. flask equipped with a stirrer, thermometer, reflux condenser, and dropping funnel, after which 58 g. (1 mol) of propylene oxide was added over a period of about 40 minutes, during which time the temperature rose from 28° C. to 68° C. The product was heated for an additional 45 minutes at 95° C., after which it was blown with nitrogen for 1 hour on the steam bath. A pale yellow concentrate was obtained, which upon analysis was found to contain 4.1% phosphorus and 7.7% sulfur.

Example 2.—Di-(methylcyclohexyl) dithiophosphoric acid-propylene oxide reaction product

A mixture of 912 g. (8 mols) of methylcyclohexanol and 444 g. (2 mols) of P_2S_5 was heated for 1 hour at 110° C. in a 3-necked 1-l. flask equipped with a thermometer, stirrer, and reflux condenser. The product (di-(methylcyclohexyl) dithiophosphoric acid) was then blown with nitrogen on the steam bath to remove H_2S.

The acid was decanted into a 4-necked 3-l. flask equipped with a stirrer, thermometer, reflux condenser, and dropping funnel, after which 232 g. (4 mols) of propylene oxide was added over a period of 1½ hours, keeping the temperature below 45° C. by means of an ice bath. Following a 45-minute soaking period at 95° C., the product was filtered, giving a clear, brown liquid which contained 8.3% phosphorus and 14.1% sulfur.

Example 3.—Di-(tert.-octylphenyl) dithiophosphoric acid-butadiene monoxide reaction product

A mixture of 824 g. (4 mols) of tert.-octylphenol and 222 g. (1 mol) of P_2S_5 was heated at 150° C. for 1½ hours in equipment similar to that employed in previous examples, followed by filtration and blowing with nitrogen. The product was di-(tert.-octylphenyl) dithiophosphoric acid.

784 g. (1.54 mols) of the acid was charged into a 4-necked, 2-l. flask equipped with a stirrer, thermometer, reflux condenser and dropping funnel. At a temperature of 70° C. 108 g. (1.54 mols) of butadiene monoxide was added over a period of two hours with rapid stirring, the temperature being maintained at 70–80° C. by means of a water bath. The product was then stirred for an additional hour at 70° C. A viscous, light brown liquid was obtained which contained 4.7% phosphorus and 9.9% sulfur.

Example 4.—Dioleyl dithiophosphoric acid-ethylene oxide reaction product

A mixture of 536 g. (2 mols) of oleyl alcohol and 111 g. (0.5 mol) of P_2S_5 was heated at 145° C. for 1½ hours. Following filtration to remove a small amount of unreacted P_2S_5, the product (dioleyl dithiophosphoric acid) was blown with nitrogen on the steam bath for 30 minutes.

The filtrate was then transferred to a 4-necked 2-l. flask equipped with a stirrer, thermometer, Dry Ice reflux condenser, and gas inlet tube. Ethylene oxide was then passed into the stirred thiophosphoric acid for 2 hours, maintaining the temperature under 30° C. both by cooling bath and slow introduction of ethylene oxide. The product was then blown with nitrogen on the steam bath for 20 minutes. A light brown liquid was obtained, which, upon analysis, was found to contain 5.2% phosphorus and 9.4% sulfur.

Example 5.—Diisopropyl dithiophosphoric acid-styrene oxide reaction product

A mixture of 120 g. (2 mols) of isopropanol and 111 g. (0.5 mol) of P_2S_5 was heated at 95° C. for 45 minutes in a 1-l. 3-necked flask equipped with a stirrer, thermometer and reflux condenser. The product (diisopropyl dithiophosphoric acid) was then filtered to remove a small amount of unreacted P_2S_5, after which the filtrate was blown with nitrogen for 30 minutes on the steam bath.

The acid was then transferred to a 4-necked, 1-l. flask equipped with a stirrer, thermometer, reflux condenser and dropping funnel. 120 g. of styrene oxide (1 mol) was then added over a period of 1 hour, keeping the temperature under 45° C. by means of a cold water bath. The reaction mixture was then stirred at room temperature for 1 hour. A pale yellow liquid was obtained which upon analysis was found to contain 8.7% phosphorus and 16.6% sulfur.

Example 6.—Di-(sulfurized oleyl) dithiophosphoric acid-ethylene oxide reaction product

Sulfurized oleyl alcohol was prepared by heating a solution of 268 g. (1.0 mol) of oleyl alcohol in 268 g. of a light mineral oil with 32 g. (1.0 mol) of sulfur at 165° C. for one hour with rapid stirring.

The oil solution of sulfurized oleyl alcohol was then heated with 55.5 g. (0.25 mol) of P_2S_5 at 145° C. for 1½ hours followed by filtration to remove a small amount of unreacted P_2S_5. The filtrate was then blown with nitrogen on the steam bath for 20 minutes. The product was an approximately 50% oil solution of di-(sulfurized oleyl) dithiophosphoric acid.

The filtrate was placed in a 4-necked, 2 liter flask equipped with a stirrer, thermometer, reflux condenser, and gas inlet tube. Ethylene oxide was then passed into the stirred solution for 2 hours, keeping the temperature below 30° C. by means of an ice bath. The reaction product was then blown with nitrogen on the steam bath for 20 minutes, a clear, reddish liquid was obtained which analyzed 2.0% phosphorus and 8.8% sulfur.

Example 7.—Di-(sulfurized tert.-octylphenyl) dithiophosphoric acid-butadiene monoxide reaction product

A mixture of 460 g. (0.5 mol) of a 50% oil solution of tert.-octylphenol sulfide (containing an average of about 1.5 atoms of S for each pair of benzene rings) and 55.5 g. (0.25 mol) of P_2S_5 was heated at 145° C. for 1 hour with rapid stirring, followed by filtration and a 20-minute nitrogen blowing period on the steam bath. The product was di-tert.-octylphenol sulfide dithiophosphoric acid.

The product was transferred to a 4-necked 2-liter flask equipped with a stirrer, thermometer, dropping funnel, and reflux condenser. 35.0 g. (0.5 mol) of butadiene monoxide was added dropwise over a period of 45 minutes, maintaining the temperature below 45° C. by means of an ice bath. After stirring for an additional hour at this temperature, the product was blown with nitrogen on the steam bath for 25 minutes. A clear, dark red,

viscous liquid was obtained which analyzed 2.6% phosphorus and 9.4% sulfur.

Example 8.—Di-(sulfurized tert.-octylphenyl) dithiophosphoric acid-styrene oxide reaction product

The di-tert.-octylphenol sulfide dithiophosphoric acid was prepared as described in Example 7.

At a temperature of 45° C., 60 g. (0.5 mol) of styrene oxide was added to the thiophosphoric acid over a period of about 45 minutes with rapid stirring. After stirring for an additional hour at this temperature, the product was placed on the steam bath and blown with nitrogen for 25 minutes. A clear, dark red, viscous liquid was obtained which analyzed 2.6% phosphorus and 8.8% sulfur.

It is to be noted in the above examples that the organo groups of the di-substituted dithiophosphoric acids contained in the range of 3–17 carbon atoms per radical were either aliphatic, alicyclic, mono-alkyl phenyl groups or sulfurized derivatives thereof. The epoxides contained 2–8 carbon atoms per molecule and were either epoxy-alkanes, epoxy-alkenes or styrene oxide.

Example 9.—S. O. D. corrosion test

Blends were prepared containing 0.25% by weight of each of the products of Examples 1 to 8 in a paraffinic mineral lubricating oil of SAE 20 grade. Where the product was obtained in the form of a mineral oil solution a quantity of the product was employed which was equivalent to 0.25% of the active compound.

These blends and a sample of the unblended base oil were submitted to a corrosion test, known as the S. O. D. corrosion test, designed to measure the effectiveness of the product 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 oils 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 or Oil Blend	Bearing Corrosion Life (Hrs.)
Base Oil	9
Base oil+0.25% product of Example 1	18
Base oil+0.25% product of Example 2	23
Base oil+0.25% product of Example 3	21
Base oil+0.25% product of Example 4	21
Base oil+0.25% product of Example 5	49
Base oil+0.25% product of Example 6	27
Base oil+0.25% product of Example 7	44
Base oil+0.25% product of Example 8	56

Example 10.—Lauson engine test

Blends containing 1% by weight of the active ingredient of each of the products of Examples 2 and 8 in a solvent extracted Mid-Continent oil of SAE 10 grade and a sample of the unblended base oil were employed as the crankcase lubricant in tests with a Lauson engine operating at 295° F. jacket temperature and 300° F. oil temperature, 1800 R. P. M. speed, and 1.5 indicated kilowatt load, the tests being conducted for 25 hours each. The loss in weight of the copper-lead bearing was determined. The results of these observations are as follows:

Lubricant	Bearing Weight Loss (mg./bearing)
Base Oil	74
Base oil+1% product of Example 2	9
Base oil+1% product of Example 8	18

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, phosphites, thiophosphates, and thiophosphites, metal xanthates and thioxanthates, metal thiocarbamates, and the like. Other types of additives, such as phenols and phenol sulfides, may also be present.

The lubricating oil base stock 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 by solvent extraction with solvents such as phenol, sulfur dioxide, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils resembling petroleum 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.

For the best results the base stock chosen should normally be an oil which with 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, no strict rule can be laid down for the choice of the base stock. The additives are normally sufficiently soluble in the base stock, but in some cases auxiliary solvent agents may be used. The lubricating oils will usually range from about 40 to 150 seconds (Saybolt) viscosity at 210° F. The viscosity index may range from 0 to 100 or even higher.

Other agents than those which have been mentioned may be present in the oil composition, such as dyes, pour point depressants, heat thickened fatty oils, sulfurized fatty oils, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, and the like.

Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having preferably 8–20 carbon atoms, e. g., octyl alcohol, lauryl alcohol, stearyl alcohol, and the like.

In addition to being employed in lubricants, the additives of the present invention may also be used in other petroleum oil products such as motor fuels, heating oils, hydraulic fluids, torque converter fluids, cutting oils, flushing oils, turbine oils, transformer oils, industrial oils, process oils, and the like, and generally as antioxidants in mineral oil products. They may also be used in gear lubricants, greases and other products containing mineral oils as ingredients.

What is claimed is:

1. A process which comprises the steps of reacting a

di-organo substituted dithiophosphoric acid with an epoxide at a temperature below 95° C. and for a period less than two hours and recovering the reaction product thereof, the organo groups of the dithiophosphoric acid containing in the range of 3–17 carbon atoms per radical and being selected from the group consisting of aliphatic, alicyclic, mono-alkyl phenyl radicals and sulfurized derivatives thereof, and said epoxide containing in the range of 2–8 carbon atoms per molecule and being selected from the group consisting of epoxy-alkanes, epoxy-alkenes and styrene oxide.

2. The process of claim 1 wherein the reaction is conducted in the presence of an inert solvent.

3. A process according to claim 1 wherein said reaction product is blown with nitrogen to remove H_2S.

4. A process according to claim 1 wherein said reaction product is recovered by filtration.

5. A process which comprises the steps of slowly adding an epoxide to a di-organo substituted dithiophosphoric acid while cooling the reaction mixture to maintain a reaction temperature in the range of 28–80° C., soaking the reaction mixture at a temperature in the range of 45–90° C. for a time in the range of 45 minutes to one hour and recovering the reaction product thereof, said epoxide containing in the range of 2–8 carbon atoms per molecule and being selected from the group consisting of epoxy-alkanes, epoxy-alkenes and styrene oxide and the organo groups of said di-organo substituted dithiophosphoric acid, each containing in the range of 3–17 carbon atoms per radical and being selected from the group consisting of aliphatic, alicyclic, mono-alkyl phenyl groups and sulfurized derivatives thereof.

6. A process which comprises the steps of slowly adding propylene oxide to an oil solution of di-(C_8 Oxo) dithiophosphoric acid while cooling the reaction mixture to maintain a temperature between about 28 to 68° C., heating the reaction mixture for an additional 45 minutes at 95° C., and blowing said reaction mixture with nitrogen for 1 hour, to form a concentrate of the reaction product.

7. A process which comprises the steps of slowly adding propylene oxide to di-(methylcyclohexyl) dithiophosphoric acid to form a reaction product while cooling the reaction mixture to maintain a temperature below 45° C., heating the reaction mixture for 45 minutes at a temperature of 95° C. to complete the reaction and filtering said reaction product.

8. A process which comprises the steps of slowly adding styrene oxide to diisopropyl dithiophosphoric acid to form a reaction product while the temperature of the reaction mixture is maintained under 45° C. by cooling, followed by stirring said reaction mixture at room temperature for 1 hour.

9. A process which comprises the steps of slowly adding butadiene monoxide to di-(sulfurized tert.-octyl phenyl) dithiophosphoric acid to form a reaction product while cooling the reaction mixture to maintain a temperature below about 45° C., stirring the reaction mixture for an additional hour at about 45° C. and blowing the product with nitrogen.

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Notice of Adverse Decision in Interference

In Interference No. 90,445 involving Patent No. 2,844,616, J. P. McDermott, PROCESS FOR REACTING DI-ORGANO SUBSTUTUTED DITHIOPHOSPHORIC ACID COMPOUNDS AND EPOXIDES, final judgment adverse to the patentee was rendered Feb. 9, 1962, as to claim 1.

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