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OXIDATION RESISTING HYDROCARBON PRODUCTS

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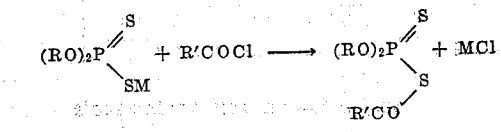
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The present invention relates to the improvement of hydrocarbon products derived from petroleum sources and more particularly to the preparation of improved mineral lubricating oil compositions by the incorporation therein of a class of additives which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

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 and other petroleum hydrocarbon products in small proportions substantially reduce the tendency of such oils to corrode the metal surfaces, particularly the surfaces of copper-lead and cadmium-silver bearings which are employed in internal combustion engines, and they are likewise effective in inhibiting oxidation of hydrocarbon products generally.

The new class of materials which have been found to possess the anti-oxidant and stabilizing properties described above are mixed anhydrides derived structurally from organo-substituted acids of phosphorus and organic carboxylic acids. These anhydrides may be conveniently prepared by reacting a metal salt of the acid of phosphorus with an organic carboxylic acid chloride, as illustrated by the following type reaction:



In the above formulas R and R' represent organic radicals and M represents a metal.

The acids of phosphorus which may be employed in preparing the mixed anhydrides may be organo-substituted thiophosphorous acids, thiophosphoric acids, thiophosphinic acids and thiophosphonic acids. The organic groups of these acids may be open chain radicals which may be long or short, straight or branched, saturated or unsaturated, and may contain attached sulfur or halogen atoms or nitro groups. The organic radicals may also be of an aromatic or aliphatic-aromatic character, and may consist of phenyl, naphthyl or other aryl radicals which may contain alkyl or other aliphatic side chains, and they may consist of sulfurized aromatic groups. Cycloaliphatic groups are also included. As is well known, the organo-substituted thiophosphorous and thiophosphoric acids may be readily prepared by reacting alcohols, mercaptans, phenols or thiophenols with sulfides of phosphorus. The corresponding thiophosphinic and thiophosphonic acids may be prepared by the Grignard reactions, as illustrated by the following equations:

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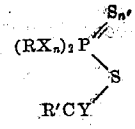
(1) Organo-thiophosphinic acid:

$$2RMgX+PCl_3 \rightarrow R_2PCl$$
$$R_2PCl+KSH \rightarrow R_2PSH+KCl$$

(2) Organo-thiophosphonic acid:

$$2RMgX+PSCl_3 \rightarrow R_2PSCl$$
$$R_2PSCl+KSH \rightarrow R_2P(S)SH+KCl$$

The organic acid halide employed in the reaction to form the mixed anhydrides of the present invention may be any carboxylic acid halide having an organic group of the character of any of the groups described in connection with the thiophosphoric acid portion of the anhydride molecule. In general, the acid halides employed may have the compositions illustrated by the formulas R'COCl or R'CSCl, where R' is a linear or cyclic hydrocarbon group, which may contain added sulfur or halogen atoms or nitro groups. The new class of anti-oxidant materials of the present invention may be more accurately defined by the general formula



Wherein R and R' are hydrocarbon radicals which may or may not have incorporated therein sulfur, halogens or nitro groups, X and Y are oxygen or sulfur, and n and n' are 0 or 1, indicating that oxygen or sulfur may be present or absent in the positions indicated.

Specific compounds useful for the purposes of the present invention may be prepared by starting with materials having organic groups of a

character falling within the scope of the compounds described above. For example, in preparing the organo-substituted acids of phosphorous, whose metal salts are to be reacted with various acid halides, a large variety of alcohols and phenols may be employed as the original starting material. Illustrative of such materials are the monohydric aliphatic alcohols, such as ethyl alcohol, isopropyl alcohol, tert.-butyl alcohol, lauryl alcohol, stearyl alcohol, wax alcohols, and alcohols obtained by the oxidation of petroleum hydrocarbons. Unsaturated alcohols, such as aleyl alcohol, and sulfurized alcohols, such as sulfurized oleyl alcohol, may be employed, as well as substituted alcohols containing halogens or nitro groups. Likewise, cyclic alcohols such as cyclohexyl alcohol may be employed. Among the phenols and naphthols may be mentioned the simple phenols as well as alkylated phenols and analogous naphthols and their derivatives and phenol sulfides formed by reacting phenols with sulfur halides.

The organic acid halides which may be employed in the preparation of the mixed anhydrides may be illustrated by any of the well known acid halides, such as acetyl chloride, stearyl chloride, benzoyl chloride, oleyl chloride, and analogous compounds. Thio-acid chlorides, in which sulfur replaces oxygen, illustrated by thioacetyl chloride, thiobenzoyl chloride, thiobutyryl chloride, and the like, may similarly be employed.

It is to be understood that not only single compounds such as metallic salts of single acids of phosphorus and single acid chlorides may be employed in the preparation of the anhydrides, but mixtures of salts and salts of mixed acids of phosphorus, as well as mixtures of acid chlorides may be employed in the preparation of anhydride products in accordance with the present invention. The products of reactions involving such mixtures will necessarily be mixtures of various anhydrides, but such anhydrides will fall within the general scope of the above definition.

For general antioxidant purposes and particularly when the additives are to be employed in mineral lubricating oils the amount of the additives will range from about 0.02% to about 3% by weight, and when the additives are to be employed to improve the load carrying capacity of a lubricant the amount will generally be somewhat greater, that is, of the order of 3% to 10% of additive.

The preparation and testing of samples of the additives of the present invention are illustrated by the examples to be described in detail below, but such examples are not to be construed as limiting the scope of the invention in any manner.

Example 1.—Preparation of isopropyl thiophosphoric-benzoic anhydride

To a stirred suspension of 47.2 g. of sodium isopropyl thiophosphate in 600 cc. of benzene contained in a 4-necked 2-liter flask equipped with a stirrer, reflux condenser, dropping funnel and thermometer, was added a solution of 28.0 g. of C_6H_5COCl in 100 cc. of benzene over a period of 45 minutes (temp. 30° C.). After heating for an additional 2 hours at 70° C. the NaCl was filtered off and the benzene removed by vacuum distillation. The final product was a clear dark red liquid containing 9.9% phosphorus and 18.2% sulfur.

Example 2.—Preparation of isopropyl thiophosphoric-acetic anhydride

This preparation was carried out in the same manner as described in Example 1, using 47.2 g. of sodium isopropyl thiophosphate and 15.7 g. of CH_3COCl. In this case, petroleum ether was used as the reaction medium and the final two hour heating period was conducted at 45° C. A clear dark red liquid was obtained containing 12.0% phosphorus and 23.2% sulfur.

Example 3.—Preparation of octyl thiophosphoric-acetic anhydride

This preparation was carried out in the same manner as described in Example 2, using 78.4 g. of potassium octyl thiophosphate (prepared from 2-ethylhexanol) and 15.7 g. of CH_3COCl. A clear pale yellow liquid was obtained containing 7.5% phosphorus and 15.3% sulfur.

Example 4.—Laboratory bearing corrosion test

Blends containing 0.25% each of the products of Examples 1 to 3 in a paraffinic type mineral lubricating oil of SAE–20 grade and a sample of the unblended base oil were submitted to a laboratory test designed to measure the effectiveness of the products 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 Blend	Bearing Corrosion Life
	Hours
Base oil	9
Base oil+0.25% isopropyl thiophosphoric-benzoic anhydride	40
Base oil+0.25% isopropyl thiophosphoric-acetic anhydride	18
Base oil+0.25% octyl thiophosphoric-acetic anhydride	18

Example 5.—Lauson engine tests

Blends containing 0.75% each of the products of Examples 1 and 2 in a solvent extracted Mid-Continent lubricating oil of SAE–10 grade and a sample of the unblended base oil were employed as crankcase lubricants in tests with a Lauson engine operated at 300° F. jacket temperature, 295° F. oil temperature, 1800 R. P. M. speed and

1.5 indicated kilowatt load, the tests being conducted for 20 hours each. The loss in weight of the copper-lead bearing was determined in each test. The results are as follows:

Oil Blend	Bearing Weight Loss (Mg./Bearing)
Base oil	220
Base oil+0.75% isopropyl thiophosphoric-benzoic anhydride	87
Base oil+0.75% isopropyl thiophosphoric-acetic anhydride	71

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 methylcyclohexyl 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. 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 material 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 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 or 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.

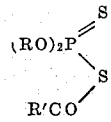
The additives of the present invention may be employed as antioxidant or stabilizing agents not only in mineral lubricating oils, but also in hydrocarbon products generally, where improved resistance to oxidation is desired. Thus the products may be added to motor oils, Diesel fuels,

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.

I claim:

1. A composition consisting essentially of a petroleum hydrocarbon product having incorporated therein 0.02% to 10% of a mixed acid anhydride of the formula—



wherein R is an alkyl radical and R′ is a radical selected from the class consisting of alkyl and phenyl radicals.

2. A composition according to claim 1 in which the petroleum hydrocarbon product is a lubricating oil fraction.

3. A composition according to claim 1 in which R is an isopropyl radical and R′ is a phenyl radical.

4. A composition according to claim 1 in which R is an isopropyl radical and R′ is a methyl radical.

5. A composition according to claim 1 in which R is an octyl radical and R′ is a methyl radical.

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