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ASHLESS DITHIOPHOSPHORIC ACID DERIVATIVES

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This invention concerns the use of an oil-soluble reaction product of a dihydrocarbon dithiophosphoric acid and a lower alkyl alcohol ester of maleic acid or of fumaric acid as an ashless additive for imparting anti-wear properties and anti-corrosion properties to lubricant compositions.

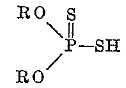
It has long been known that derivatives of dihydrocarbon dithiophosphoric acids exhibit anti-wear, anti-corrosion and antioxidant properties when incorporated into lubricating oils and related compositions. The dihydrocarbon dithiophosphoric acids are normally prepared by reacting an organic hydroxy compound such as an aliphatic alcohol, a cyclic aliphatic alcohol or a phenol with a sulfide of phosphorus, particularly with P_2S_5. The metal salts such as the nickel, lead, cadmium, and zinc salts of organic dithiophosphoric acids have in particular been found useful as anti-wear additives. The most commonly used anti-wear additives for crankcase lubricating oils are the zinc salts of dialkyl dithiophosphoric acids derived from aliphatic alcohols of from about 3 to about 12 carbon atoms, as for example from a mixture of C_4 and C_5 aliphatic alcohols.

In recent times, it has been recognized that additives for crankcase lubricants should be free, or at least relatively free, of metal content because there is a tendency for conventional metal-containing additives such as metal organo sulfonates, metal salts of alkyl phenol thioethers and the like to leave an ash residue which tends to accumulate in the combustion chamber of the engine and there cause preignition, valve burning, spark plug fouling and similar undesirable conditions. While suitable ashless pour point depressants, viscosity index improvers, detergents and dispersants have been developed for crankcase lubricants, there still remains a need for an acceptable ashless anti-wear additive.

Inasmuch as the sulfur and phosphorous contents of metal dialkyl dithiophosphoric acid salts appear to be the principal contributing factors to the anti-wear, load carrying and antioxidant functions of metal dialkyl dithiophosphates, a number of attempts have been made to prepare nonmetallic derivatives of dialkyl dithiophosphoric acids, because such derivatives would still retain the sulfur and phosphorus contents. Many of these attempts have been in the direction of neutralizing the dialkyl dithiophosphoric acids with alkylene amines such as ethylene diamine, treating the acids with alkylene oxides such as ethylene oxide or propylene oxide, or converting the dialkyl dithiophosphoric acids to polysulfides. Although many of these derivatives do exhibit fairly satisfactory anti-wear properties, the derivatives have other disadvantages, one of them being corrosivity toward the copper-lead bearings that are frequently used in engines. Another disadvantage to some of these derivatives is that they tend to be unstable and to liberate hydrogen sulfide on standing or during use.

The present invention is based upon the discovery that oil-soluble adducts of dihydrocarbon dithiophosphoric acids and aliphatic alcohol esters of maleic acid or of fumaric acid are ashless additives that exhibit good anti-wear properties and are at the same time not corrosive toward copper-lead bearings. In addition, they have good stability against hydrolysis and are also stable against evolution of hydrogen sulfide. These oil-soluble adducts are particularly effective as anti-wear additives in fully formulated lubricants that are substantially ash free, i.e. that contain ashless dispersants and do not have a metal content that exceeds about 0.01 wt. percent of sulfated ash.

The dihydrocarbon dithiophosphoric acids that are used in preparing the adducts of the present invention include those of the formula

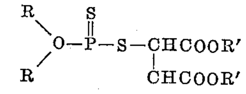


(1)

wherein R represents the same or different hydrocarbon radicals including aryl, alkyl, aralkyl and cycloalkyl radicals. These radicals may have from 1 to 20 carbon atoms, preferably 1 to 12 carbon atoms each. Most preferably R represents alkyl groups. The total number of carbon atoms in the combined R radicals should be sufficient so that the adduct formed from the dihydrocarbon dithiophosphoric acid will be soluble in the lubricating oil. Examples of such dihydrocarbon dithiophosphoric acids include diisobutyl dithiophosphoric acid, lauryl phenol dithiophosphoric acid, mixed ethyl isopropyl dithiophosphoric acid, ditertiary octyl dithiophosphoric acid, mixed isopropyl C_8 oxo dithiophosphoric acid, dilauryl dithiophosphoric acid, mixed isobutyl primary amyl dithiophosphoric acid, diphenol dithiophosphoric acid, mixed dithiophosphoric acids derived from mixed alcohols from paraffin wax oxidation, mixed hexyl stearyl dithiophosphate, mixed isopropyl C_{18} oxo dithiophosphoric acid and mixed dithiophosphates derived from mixed C_{10} to C_{18} alcohols known as "Lorol" alcohols and so forth.

The aliphatic alcohol esters of maleic acid or of fumaric acid that are employed in preparing the adducts of this invention are preferably those derived from aliphatic alcohol of from 1 to 10 carbon atoms. These include methyl maleate, isopropyl fumarate, butyl maleate, nonyl fumarate, amyl maleate and the like.

The preparation of adducts of dihydrocarbon dithiophosphoric acids and aliphatic esters of maleic acid or of fumaric acid may follow the procedure described in U.S. Patent 2,578,652. Briefly, this involves the reaction of more or less equimolar proportions of the two reactants at a temperature in the range of from about 60° to about 300° F. or more particularly, from about 100° to about 180° F. The reaction time may be as short as four hours or as long as several days, depending somewhat on the reaction temperature. Polymerization of the fumarate or maleate ester may be guarded against by including about 0.05 to about 0.3 wt. percent (based on the total weight of reactants) of an inhibitor such as hydroquinone. The reaction may be promoted with an aliphatic tertiary amine catalyst such as trimethyl amine or tri-n-butyl amine. It is believed that the adduct is formed by attachment of the acidic sulfur atom of the dithiophosphoric acid to the double bond of the maleic acid ester or fumaric acid ester. The resulting adduct may be represented by the general formula:



(2)

wherein R has the same significance as in Formula 1 above and R′ represents the aliphatic portion of the starting maleic acid or fumaric acid ester.

The additives of this invention may be employed in concentrations ranging from about 0.01 to about 10 wt. percent in lubricating oil compositions. The additives may be incorporated directly into the lubricant compositions by simply adding them with mixing; applying heat if necessary to facilitate solution. In some cases concentrates, containing for example in the range of from 20 to 80% of additive on an active ingredient basis the balance being an oil base, may first be prepared for convenience in handling the additive for ultimate blending into a finished lubricating oil composition.

For use in crankcase lubricants, the products of this invention will be used in concentrations of about 0.1 to about 10 wt. percent or more commonly in concentrations of from about 0.2 to about 5 wt. percent. The lubricating oil base stocks include not only mineral lubricating oils but also synthetic oils. In addition to synthetic hydrocarbon lubricating oils, other synthetic oils include dibasic acid esters such as di-2-ethylhexyl sebacate, carbonate esters, phosphate esters, halogenated hydrocarbons, polysilicones, polyglycols, complex esters and the like.

Although the invention is primarily concerned with improved crankcase lubricants, it is also applicable to other lubricant uses where wear may be a problem, as for example in turbine oils, transmission fluids, hydraulic oils, and the like.

Other ocnventional additives that may also be present in the lubricant compositions include dyes; pour point depressants such as wax alkylated naphthalene; antioxidants such as 2,6-ditertiary butyl p-cresol, phenyl alpha naphthyl amine, tertiary octyl phenol sulfide, bisphenols; ashless sludge dispersants; viscosity index improvers such as polymethacrylates, polyisobutylene, alkyl fumarate-vinyl acetate copolymers; and the like.

The present invention is particularly applicable to the preparation of a fully formulated ashless crankcase lubricant containing an effective amount (e.g. 0.1 to 10 wt. percent) of an ashless dispersant. The lubricant composition may also contain an ashless viscosity index improver such as an olefin polymer, an acrylate ester polymer, or the like. Ashless dispersants that may be used include the imide reaction product of an alkenyl succinic anhydride with an aliphatic polyamine such as described, for example, in Canadian Patent 666,916. Ashless dispersants that also provide viscosity index improvement may be used. These include high molecular weight polymeric dispersants having polar groups such as a copolymer of 65 to 85 wt. percent of mixed C_9 to C_{12} fumarates, 10 to 20 wt. percent of vinyl acetate and 5 to 15 wt. percent of N-vinyl pyrrolidone. Another example is the copolymer derived by reaction of mixed C_{16} to C_{18} fumarate esters and C_8 oxo alcohol fumarates with vinyl acetate in a ratio of 3:1 acetate to fumarate, along with 3 wt. percent of maleic anhydride, followed by subsequent removal of excess vinyl acetate. A preparation of this type is disclosed in U.S. Patent 3,136,743.

As previously stated, an ashless lubricant is considered to be one that contains no more than 0.01 wt. percent of sulfated ash.

The nature of the invention and the benefits derived from the practice thereof will be more fully understood when reference is made to the following examples.

Example 1

A high detergency lubricating oil base composition suitable as a crankcase lubricant with the exception that no anti-wear additive was present was formulated by simple mixing of 2300 volumes of a solvent neutral lubricating oil fraction of 100 SSU viscosity at 100° F., 235 volumes of a solvent neutral lubricating oil of 450 SSU viscosity at 100° F., 316 volumes of a polyisobutylene V.I. improver concentrate, 113 volumes of an ashless dispersant concentrate and 16 volumes of a pour point depressant concentrate. The pour point depressant concentrate was a 50% solution in diluent oil of a mixture of a wax alkylated naphthalene and a C_{10} to C_{18} alkyl-fumarate-vinyl acetate copolymer, and the viscosity index improver was a 20 volume percent concentrate in mineral oil of 15,000 molecular weight polyisobutylene. The ashless dispersant was a 70 wt. percent concentrate in mineral oil of an imide condensation product of about equimolar proportions of tetraethylene pentamine and an alkenyl succinic anhydride which was derived by condensation of polyisobutylene of about 1000 molecular weight with maleic anhydride. The resultant composition had a viscosity at 100° F. of 329 SSU, a viscosity at 210° F. of 63.5 SSU and a pour point of −15° F.

Using the base oil composition just described, two fully formulated crankcase lubricants were prepared. In one case, one part by weight of a zinc dialkyl dithiophosphate anti-wear additive concentrate was added by simple mixing to 142 parts by weight of the base oil formulation. In the other case, one part by weight of an adduct of dimethyl dithiophosphoric acid and diethyl maleate was added by simple mixing to 142 parts by weight of the base oil formulation. The latter adduct was a commercial product known as Malathion. The zinc dialkyl dithiophosphate concentrate was an oil solution consisting of about 25 wt. percent of mineral lubricating oil and about 75 wt. percent of zinc dialkyl dithiophosphate prepared by treating a mixture of isobutanol and mixed amyl alcohols with P_2S_5 followed by neutralizing with zinc oxide. Inspection data and laboratory test performance data on these two formulations are given in the following Table I.

TABLE I

Inspections	Composition Containing—	
	Zinc Additive	Adduct of Present Invention
Sulfated Ash, wt. percent	0.19	0.03.
Zinc, wt. percent	0.06	0.
P, wt. percent	0.053	0.062.
S, wt. percent	0.26	0.25.
N, wt. percent	0.11	0.11.
Vis./100° F., SSU	331.8	329.1.
Vis./210° F., SSU	63.6	63.5.
API Gravity	32.1	31.9.
Copper Strip Test	Clean	Clean.
H_2S Test 1 Hour/100° F	0	0.
Falex Wear, mg	2.4	1.6.
Lubricant Hydrolysis:		
H_2S/30 min	Test paper tan	Test paper white.
Steel Strip/16 hrs	Black rust	No rust.

The Falex wear test data given in Table I were obtained by running the test compositions in a Falex wear test machine for 30 minutes at 500 lbs. direct gauge reading. The copper strip test was the standard ASTM test involving immersion of copper strips in the oils under test for three hours at 210° F. and then noting the appearance of the strips.

The H_2S test is also a standardized test wherein a capped 4-ounce narrow mouth bottle containing 82 grams of the oil under test is placed in an oven for one hour at 100° F.; then lead acetate test paper is held over the neck of the uncapped bottle for five minutes to determine the presence of H_2S.

The laboratory hydrolysis test is conducted by mixing the test oil with 10 vol. percent of water and placing the mixture in a tall glass tube and then bubbling air through the tube while the mixture was kept at a temperature of 160° F. Steel strips are placed in the glass tubes for their full length so that half of the strip is immersed in the oil and water mixture and the other half is in the space above the liquid. The appearance of the strips is noted at the end of sixteen hours. The test for H_2S evolution in the laboratory hydrolysis test is made at the end of thirty minutes by holding a piece of lead acetate paper at the top of the tube.

It will be noted from the test data in Table I that the additive of the present invention was superior to the conventional zinc dialkyl dithiophosphate with respect to wear reduction and with respect to hydrolytic stability.

A CLR–L–38 engine test was conducted on the detergent base oil composition and two duplicate tests were conducted on each of the complete motor oil formulations described above. These tests were run in a 1-cylinder Labeco engine operating for forty hours in each test.

This engine had conventional copper-lead bearings. The results of these five tests are given in the following Table II.

TABLE II.—L–38 ENGINE TESTS

Oil Containing:	Bearing weight loss, Mg.
Zinc dialkyldithiophosphate	90.2, 95.6
Dithiophosphoric acid maleate	86.3, 67.0
No antiwear additive	856.6

It will be noted from the data in Table II that the adduct of the present invention was better in reducing the corrosive tendencies of the base oil than was the conventional zinc dialkyldithiophosphate.

Both of the fully formulated motor oils described above were also tested for effectiveness as crankcase lubricating oils in new Dodge 6-cylinder taxicabs operating in regular service in New York City. Before starting the tests, the valve lifters from each of the taxis were removed, measured, and then replaced in the engine. At the end of the test period, which was of the order of 6000 to 7000 miles, the valve lifters were again removed from the engines and measured and the average lifter wear was thereby determined. The engines were at the same time inspected for sludging tendencies by examining several of the parts that come into contact with the crankcase oil, including the rocker arm assembly, the push rod chamber, the crankshaft, and the oil pan. These parts were visually and quantitatively rated for sludge deposits using a sludge merit rating system in which a numerical rating of 10 represents a perfectly clean part and the numerical scale decreases to a minimum value representing a part covered with the maximum amount of sludge possible. Two taxicabs were used for each oil in the comparative tests. The results of the tests are summarized in the following Table III.

TABLE III

Taxi No.	Miles	Composition Containing	Average Lifter Wear, Inch $\times 10^{-4}$	Sludge Rating
1	6,889	Zinc Dithiophosphate	22	9.8
2	6,510	do	17	9.5
3	6,730	Dithiophosphoric Acid Adduct	17	9.8
4	6,217	do	14	9.7

It will be seen from the data in Table III that the adduct additive of the present invention is a useful substitute for the conventional zinc dialkyldithiophosphate anti-wear additive, since it enables the formulation of a completely ashless crankcase lubricant in which there is no adverse effect on other desirable properties of the lubricant including freedom from sludge formation.

Example 2

An ashless high detergency crankcase lubricating oil is formulated by adding the base oil composition of Example 1, 0.9 wt. percent of the adduct of diisopropyl fumarate and a mixed dialkyl dithiophosphoric acid that has been prepared by reaction of P_2S_5 with a mixture of isobutanol and mixed primary amyl alcohols. The adduct has been prepared by heating a mixture of approximately equimolar proportions of the fumarate and the dithiophosphoric acid for 20 hours at 150° F.

Comparative example

A high detergency lubricating oil base composition suitable as a crankcase lubricant, with the exception that it contained no anti-wear additive, was prepared by simple mixing of 5.8 wt. percent of a detergent additive concentrate, 2.5 wt. percent of a barium sulfonate concentrate, 2.1 wt. percent of an ashless dispersant concentrate, 6.7 wt. percent of a viscosity index improver and 82.9 wt. percent of a refined solvent neutral mineral lubricating oil of 150 SSU viscosity measured at 100° F. The detergent additive concentrate was a 50 wt. percent concentrate

in mineral oil of an additive prepared by reacting a mixture of phosphosulfurized polyisobutylene and nonyl phenol with barium hydroxide pentahydrate and blowing the mixture with CO_2. The metal content of the concentrate was about 10.6 wt. percent as BaO. The barium sulfonate concentrate was a 45 wt. percent concentrate of a high alkalinity barium synthetic sulfonate and had a total base number of 59 and contained 14.5% Ba. The viscosity index improver was a 40,000 molecular weight copolymer of 50 mole percent vinyl acetate and 50 mole percent of mixed C_8–C_{16}–C_{18} alcohol fumurate esters. The ashless dispersant was the same as that used in Example 1.

Comparative blends were prepared by adding respectively to separate portions of the base composition just described 1.2 wt. percent of the zinc dialkyl dithiophosphate concentrate described in Example 1 and 1 wt. percent of Malathion (dimethyl dithiophosphoric acid—diethyl maleate adduct). Each of these compositions was subjected to the Falex wear test described in Example 1. The test results obtained are given in the following Table IV along with the Falex test data of Table I.

TABLE IV.—FALEX WEAR TEST RESULTS

[30 minutes at 500 lbs. direct load]

	Mg. of wear	
	Ashless Base	Metal-Containing Base
Base Oil Plus:—		
Zinc salt	2.4	3.0
Adduct of Present Invention	1.6	23.6
Base Oil Alone	(1)	(1)

[1] Break, weld.

It will be seen from the data of Table IV that the adduct of the present invention is not as effective in reducing wear as the zinc dialkyl dithiophosphate in a lubricant compounded with metal-containing detergents whereas it is appreciably more effective than the zinc salt in a lubricant compounded with essentially metal-free additives. In each case there was film rupture and seizing when the base oil was run without either of the anti-wear additives.

It is to be understood that the examples embodying the present invention are intended to be merely illustrative of the invention and that modifications and variations thereof can be employed without departing from its scope as defined in the appended claims.

What is claimed is:

1. A lubricating oil composition comprising a major proportion of a hydrocarbon lubricating oil of internal combustion engine crankcase oil viscosity grade to which has been added from 0.01 to 10 wt. percent of an adduct that has been prepared from a dihydrocarbon dithiophosphoric acid having hydrocarbon radicals of from 1 to 20 carbon atoms and from an ester of a C_1 to C_{12} aliphatic alcohol and an unsaturated dicarboxylic acid selected from the group consisting of maleic acid and fumaric acid.

2. A lubricating oil composition as defined by claim 1 which additionally contains a sludge dispersing amount of an ashless dispersant additive.

3. A lubricating oil composition as defined by claim 1 wherein the metal content of the composition does not exceed 0.01 wt. percent of sulfated ash.

4. A lubricating oil composition comprising a major proportion of a hydrocarbon lubricating oil of internal combustion engine crankcase oil viscosity grade and from 0.01 to 10 wt. percent of an adduct prepared by the reaction of a dialkyl dithiophosphoric acid wherein the alkyl groups contain from 1 to 10 carbon atoms with a C_1 to C_{12} aliphatic alcohol ester of maleic acid, said composition being substantially devoid of metal-containing additives.

5. A lubricating oil composition as defined by claim **4** wherein said adduct has been derived from dimethyl dithiophosphoric acid and diethyl maleate.

6. A lubricating composition as defined by claim **4** which has been prepared from diisopropyl fumurate and mixed C_4–C_5 dialkyl dithiophosphoric acids.

7. A method for reducing wear in the operation of an internal combustion engine which includes the step of employing as the crankcase oil for that engine a substantially metal-free lubricating oil composition comprising a major proportion of a hydrocarbon lubricating oil of internal combustion engine crankcase oil viscosity grade to which has been added from 0.1 to 10 wt. percent of an adduct prepared by the reaction of a C_1 to C_{12} alcohol ester of maleic acid with a dialkyl dithiophosphoric acid wherein the alkyl groups contain from 1 to 10 carbon atoms.

8. A fully compounded crankcase lubricating oil of internal combustion engine crankcase oil viscosity grade comprising a major proportion of a hydrocarbon lubricating oil, a minor viscosity index improving amount of a substantially metal-free viscosity index improver, a minor effective amount of a substantially metal-free dispersant and from 0.1 to 10 wt. percent of an adduct that has

been prepared from a dihydrocarbon dithiophosphoric acid having hydrocarbon radicals of from 1 to 20 carbon atoms and from an ester of a C_1 to C_{12} aliphatic alcohol and an unsaturated dicarboxylic acid selected from the group consisting of maleic acid and fumaric acid, said lubricant having a total metal content that does not exceed 0.01 wt. percent of sulfated ash.

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