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LUBRICANT COMPOSITIONS CONTAINING MIXED DITHIOPHOSPHORIC DICARBOXYLIC ACID ANHYDRIDES AND SUBSTITUTED AMINE DETERGENTS

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ABSTRACT OF THE DISCLOSURE

Lubricant composition containing an alkenyl succinimide or aliphatic hydrocarbon substituted amine detergent additive and as a corrosion inhibitor, a mixed anhydride of a dicarboxylic acid and a dihydrocarbyl dithiophosphoric acid.

This application is a continuation-in-part of application Ser. No. 354,761, filed Mar. 25, 1964 and now abandoned.

This invention relates to improved lubricant compositions. Most specifically, it relates to lubricant compositions which display superior oxidation and corrosion resistance as well as excellent detergency characteristics and incorporate nitrogen-containing detergent additives in combination with novel mixed dithiophosphoric-dicarboxylic acid anhydrides.

Within recent years, it has become common practice to impart improved properties to lubricants by the addition of certain additives or addition agents. Of particular importance in the operation of internal combustion engines is the use of certain compounds which function to prevent the accumulation of deposits such as varnish-like coatings on the pistons, cylinder walls and other operating parts of the engine. These compounds which act to disperse accumulated solids in the oil are known as dispersant or detergent type additives.

Among the more successful detergent additives which have been introduced are the oil-soluble, high molecular weight basic nitrogen-containing compounds. Outstanding examples of these compounds are the alkenyl succinimides and the polyolefin substituted polyamines of the type disclosed in U.S. Patent 3,275,554. These compounds possess superior detergent characteristics and are employed in a variety of lubricant compositions.

A further problem encountered in the utilization of any lubricating oil in an internal combustion engine is a deterioration of the oil resulting in the formation of highly corrosive substances. These materials attack metal surfaces of engines, deteriorating engine oil and causing severe operational problems in normal engine usage. Particularly susceptible to corrosive attack are the alloy metal (usually copper-lead) bearings employed in modern internal combustion engines.

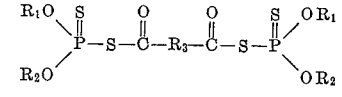
Therefore, it has been found necessary to add to modern lubricating compositions, materials which function to reduce corrosive attack engendered by the oxidative decomposition products. Thus, a great number of materials have been utilized to perform this function, and many highly successful anti-corrosives are known in the art.

However, a particular problem is encountered when the substituted amine detergent type additives previously referred to are employed. For this reason auxiliary anti-

corrosive compounds may be used with this type of detergent and result in a composition having improved non-corrosive characteristics. Unfortunately, decreased detergent activity of the composition often results.

Phthalic acids, especially isophthalic and terephthalic acids, have previously been found to function unusually well as corrosion inhibitors, while at the same time preserving detergent characteristics. The use of these compounds is described in Stewart et al. U.S. Patent 2,809,160. These compounds are highly effective anti-corrosives and may be combined successfully with numerous kinds of lubricating oil bases and with other lubricant additives. Their use in combination with the class of oil-soluble high molecular weight substituted amine-containing detergent additives previously described often results in an increase in the amount of varnish and other carbonaceous materials deposited upon valves, piston skirts and on piston ring grooves. Thus the elimination or reduction of the tendency to form these deposits with retention of anti-corrosive characteristics when employed with varieties of oils and other additives is a primary object of this invention.

It has now been found that new and superior lubricant compositions displaying excellent non-corrosive and non-deposit forming characteristics can be prepared from a major proportion of an oil of lubricating viscosity in combination with a substituted amine detergent additive, said combination being corrosive to metal surfaces in normal use, and a minor portion sufficient to inhibit corrosion of a mixed anhydride of the general formula:



wherein R_1 and R_2 represent hydrocarbon radicals selected from the group consisting of alkyl, alkyl phenyl radicals, and mixtures thereof, and R_3 is selected from the group consisting of aliphatic and aromatic divalent hydrocarbon radicals.

Thus the inhibitors of this invention comprise two units of a hydrocarbon diester of a thiophosphoric acid group and one unit of an aromatic or alkyl dicarboxylic acid arranged in a bis structure. Suitable hydrocarbon groups which may be attached by the ester linkage to the dithiophosphate radical are straight or branched chain alkyl groups containing from 4 to 18 carbon atoms and alkyl phenyl groups having from 8 to 24 carbon atoms in the alkyl chain. Suitable dicarboxyl groups include straight and branched chain alkyl and aromatic mono or multinuclear hydrocarbons. Especially suitable are terephthalic and isophthalic acids. When the dicarboxylic acid is terephthalic, the ester groups are preferably aliphatic and when the acid is isophthalic the ester groups are preferably alkyl phenyl. A preferred species of the inhibitor is isophthaloyl bis O,O-dialkyl-phenyl phosphorodithioate in which the alkyl phenyl groups each have an average of 13 alkyl carbon atoms.

The inhibitors are employed in amounts sufficient to inhibit corrosion. In general, amounts from 0.001% to 10% by weight are sufficient. An amount from 0.01% to 3.0% by weight is preferred.

The detergents employed in the compositions of this invention are recently developed nitrogen-containing non-

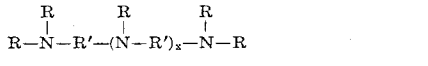
metallic ashless detergents. Examples of such detergents are those derived from alkenyl succinic anhydrides having 30, preferably 50, or more carbon atoms in the alkenyl group and amine compounds such as tetraethylene pentamine, N-aminoethyl piperazine, dimethylaminopropylamine, etc. The detergent additive is obtained by heating one mole of an alkenyl succinic anhydride with at least 0.5 mols of an amine.

The substituted succinic anhydrides contemplated as reactants in the process can be readily obtained by heating maleic anhydride with a high molecular weight olefin or with a chlorinated high molecular weight olefin at a temperature from about 150–200° C. Typical high molecular weight olefins which can be so employed are polyethylene, polypropylene, polyisobutylene, etc. Polyisobutylene is preferred.

Examples of suitable polyalkylene polyamine reactants are ethylene diamine, diethylene triamine, tetraethylene pentamine, and the like. Tetraethylene pentamine is a preferred polyamine reactant.

A preferred embodiment of the detergent additive is the product obtained by heating one mole of a polyisobutenyl succinic anhydride having about 65 carbon atoms in the olefin chain with 0.9 mols of tetraethylene pentamine.

Another class of substituted amine detergents with which the corrosion inhibitors of this invention are particularly effective are the aliphatic hydrocarbon-substituted polyamines, particularly polyolefin substituted polyamines which are exemplified, as noted, by the disclosure of U.S. Patent 3,275,554. These materials may be basically described by the formula:



wherein R′ is an alkylene group of 1 to 8 carbon atoms, R is hydrogen or an aliphatic hydrocarbon radical of from about 425 to 50,000 molecular weight, and x is an integer of 0 to 5, and at least one R is an aliphatic hydrocarbon radical. The preferred aliphatic hydrocarbon radicals are derived from polyolefins such as polyethylene, polypropylene, polybutylene, etc.

The amines from which the additives are derived include aliphatic amines and are preferably polyalkylene polyamines in which the alkylene group is of 1 to 8 carbons. Examples of these materials are ethylene diamine, diethylene, or, in other words, the same polyalkylene polyamines used to form the alkenyl succinimides previously disclosed.

The detergent additive is employed in the lubricant composition in an amount sufficient to impart detergency. Generally, amounts from 0.1 to 10% by weight are preferred.

These additives are a class of chemical compounds recognized in the art as possessing the ability to enable a lubricating oil medium to maintain oxidation products, resins, and other insoluble material in suspension or otherwise dispersed in the medium. Compositions in which these additives are employed are normally rendered more corrosive, probably due to the removal of naturally formed protective films from the sliding surfaces. Thus the use of a compatible and efficient corrosion inhibitor with these types of compounds is especially desirable.

Any of the well-known types of lubricating oils can be used as the base oil for the compositions of this invention. These oils are corrosive to metal surfaces under normal operating conditions. Examples of such base oils are naphthenic base, paraffin base, and mixed base mineral oils; synthetic oils, for example, alkylene polymers, such as polymers of propylene, butylene, etc., and mixtures thereof; alkylene oxide type polymers; dicarboxylic acid esters; phosphorus esters; silicon esters such as silicates and polysiloxanes; and alkyl aromatic hydrocarbons.

The additives of this invention are effective in lubricant

compositions containing additional conventional additives, such as oxidation inhibitors, supplementary detergents, sludge inhibitors, pour depressants, V.I. improvers, antifoaming agents, rust inhibitors, oiliness agents, wear inhibitors, dyes, etc.

The inhibitors of this invention may be prepared by any suitable method such as a reaction of the sodium, potassium, or lead salts etc. of the dithiophosphates with aroyl or acyl halides. However, a particularly suitable method utilizing the pyridine salt of the dithiophosphoric acid will be described in the following examples. The examples are intended to be only illustrative and not limiting of the invention.

Example I.—Preparation of the mixed anhydride of terephthalic acid and di (alkylphenyl) dithiophosphoric acid

0.4 mol of a di (alkylphenyl) dithiophosphoric acid having an average of 13 alkyl carbons on each phenyl group, the material being in oil solution, 32 grams of pyridine (0.4 mol), and 115 milliliters of benzene were charged to a 2-liter, 3-necked flask equipped with a stirring unit, thermometer, addition funnel, and heating means. From the addition funnel was slowly added a solution containing 40.6 grams (0.2 mol) of terephthaloyl chloride and 200 milliliters of benzene. The mixture was stirred at room temperature for 6 hours and at 125–135° F. for 12 hours. The mixture was allowed to stand overnight and the pyridine hydrochloride was filtered from the solution. Upon removal of the solvents under reduced pressure, a viscous reaction product was obtained. Analysis showed 2.76% phosphorus; theory=2.71%. Analysis observed 6.6% sulfur; theory=5.59%.

Example II.—Preparation of the mixed anhydride of terephthalic acid and mixed isobutyl primary amyl dithiophosphoric acid

123 grams of an oil solution of dialkoxy dithiophosphoric acid (alkoxy residue=63.6% isobutanol, 36.4% mixed primary amylols, average molecular weight alcohols=79.2) (0.4 mols), 32 grams of pyridine (0.4 mols), and 200 milliliters of benzene were placed in a 2-liter, 3-necked flask equipped with stirring unit, addition funnel, thermometer, and a heating means. Through the addition funnel was added a solution containing 40.6 grams (0.2 mols) of terephthaloyl chloride and 200 ml. of toluene and 100 ml. of benzene. The mixture was stirred at room temperature for 10 hours and at 125–150° F. for 6 hours. After filtering of the pyridine hydrochloride, the solvent was removed at a reduced pressure. A viscous dark-reddish product was obtained. Analysis showed 8.2% phosphorus and 17.1% sulfur. Theoretical phosphorus in the pure compound, free of oil, is 9.6%.

The oxidation inhibition characteristics of the compound of this invention were ascertained in an oxidation test. A 1% portion of the inhibitor was placed in a lubricating oil base which was a solvent-refined paraffinic neutral oil of SAE 30 grade containing 3.0% by weight of a polybutenyl succinimide detergent additive. The detergent was prepared by heating 1 mol of polybutenyl succinic anhydride having about 65 carbon atoms in the alkenyl chain with 0.9 mols of tetraethylene pentamine. The viscosity at 100° F. of the oil solution was determined and the oil was heated in the presence of iron and copper naphthenate catalysts at 340° F. for 20 hours. The viscosity of the oil solution at the end of the period was determined and the increase in percent recorded. These data are set out in Table I.

The corrosion inhibition properties of the compositions were determined by heating samples which corresponded to those used in the oxidation inhibition tests and measuring the weight loss of a strip of copper-lead bearing metal which was placed in the oil. The composition was aerated at a constant rate during the test period. The data are also found in Table I.

Table I.—OXIDATION AND CORROSION BENCH TESTS

Hydrocarbyl phosphorodithioate	Dicarboxylic Acid	Oxidation Test, Viscosity Increase at 110° F.	Corrosion Test Cu-Pb Wt. Loss, mg.
None	None [1]	3,300	180
Polypropylene phenyl having 13 alkyl carbons on each phenyl.	Terephthalic	41	16
Do	Isophthalic	0	5
Do	Phthalic	8	33
Do	Azelaic	0	27.2
Mixed Isobutyl-prim-amyl (63% isobutyl, 34.4% amyl).	Terephthalic	0	8.9
Do	Isophthalic	8.3	48.6

[1] Base oil alone.

As shown by the above data the dicarboxylic dithiophosphates of this invention perform efficiently as oxidation inhibitors particularly reducing viscosity increase of the oil. In addition, the corrosion tests indicate that these compounds also significantly reduce copper-lead corrosion of the base oil compositions. The isophthaloyl bis(polypropylenephenyl) phosphorodithioate and the terephthaloyl bis(mixed isobutyl isobutyl-amyl) phosphorodithioates are especially effective in reducing oxidation and corrosion.

The following test was performed illustrating the efficacy of the mixed anhydride in reducing corrosion in combination with an aliphatic hydrocarbon substituted polyamine. A solution was prepared employing in a California paraffin base oil, 2% by weight of a polyisobutylene polyalkylene polyamine (2700 mol. wt. polyisobutylene with tetraethylene pentamine). A portion was used as a control and a second portion was combined with the mixed anhydride of terephthalic acid and the phosphorodithioate of polypropylene phenyl, having an average of 13 carbon atoms in the polypropylene group to provide a concentration based on phosphorus of 36 millimols per kg. copper and lead strips, were carefully cleaned and weighed. The two oil solutions were heated to 340° F., and the copper and lead strips were immersed in each of the samples. After 20 hours, the strips were removed and cleaned with hydrocarbon solvents to remove oil. The copper strips were washed with a dilute aqueous potassium cyanide solution to remove any copper scale. The strips were then dried and weighed. The strips immersed in the control lost a total of 887.8 mg. The strips in the sample containing the mixed anhydride inhibitor lost a total of 57.1 mg.

The test was repeated employing 2% octadecyl amine instead of the hydrocarbon polyamine, giving 1717.8 mg. weight loss. This illustrates the efficacy of the anhydrides in reducing the corrosion caused by amine compounds.

The L–4 engine test was utilized to determine the corrosion inhibition and deposit forming characteristics of the composition under operational conditions. The compositions subjected to the test were similar to those used in the oxidation and bench test, i.e. containing 3% of the same detergent and 1% of the phosphorodithioate. A brief description of the test follows.

In the L–4 test, the corrosion and deposit forming characteristics of the lubricant compositions are determined in a Chevrolet standard 6-cylinder engine. Weighed copper-lead test bearings and new piston rings are installed in the engine. The test is run at a constant engine speed of about 3,000 r.p.m. under a load of 30 brake horsepower for a period of 36 hours after a run-in period of 8 hours. The outlet temperature of the jacket coolant is about 200° F. and the oil sump temperature about 280° F. At the conclusion of the test the engine is dismantled and the pistons are removed and inspected for varnish deposits and rated for cleanliness on a basis of 0 to 10, 10 being perfectly clean. The bearings are weighed to determine total weight loss due to corrosion. Table II describes the result of tests performed comparing the additives of this invention with terephthalic acid and with unhibited oil.

TABLE II.—L–4 ENGINE TEST

Inhibitor	Bearing Weight Loss (mg.)	Piston Varnish Rating
None	3,512	10.0
Terephthalic Acid	282	8.6
Terephthaloylbis (dipolypropylenephenyl) phosphorodithioates (13 alkyl carbons per phenyl group)	502	9.6

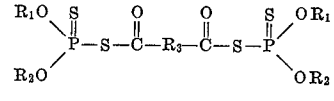
As shown by the above data, the terephthaloyl phosphorodithioate compares favorably with terephthalic acid in its ability to reduce bearing corrosion when employed in combination with this class of nitrogen-containing detergents. In addition, it shows a decided superiority in the fact that the deposit-forming characteristics of the composition are not significantly altered. Thus the varnish rating of the engine is depreciated only slightly (10.0 to 9.6 as contrasted to the depreciation of 10.0 to 8.6 for the terephthalic inhibitor). Thus the compositions of this invention provide excellent corrosion inhibition under actual operation and aid in obtaining extremely high engine cleanliness ratings.

The L–4 engine test is more fully described in the CRC Handbook, 1946 edition, Coordinating Research Council, New York, N.Y.

While the character of this invention has been described in detail with numerous examples, this has been done by way of illustration only and without limitation of the invention. It will be apparent to those skilled in the art that numerous modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the appended claims.

I claim:

1. A lubricant composition comprising a major proportion of an oil of lubricating viscosity, a minor portion sufficient to impart detergency, of an alkenyl succinimide or an aliphatic hydrocarbon substituted amine detergent additive and a minor portion sufficient to inhibit corrosion of a mixed anhydride of the general formula:



wherein R_1 and R_2 represent hydrocarbon radicals selected from the class consisting of alkyl and alkyl phenyl radicals and mixtures thereof, and R_3 is selected from the

group consisting of aromatic and aliphatic divalent hydrocarbon radicals.

2. The lubricant composition of claim 1 in which R_1 and R_2 are alkyl radicals of 1 to 12 carbon atoms and mixtures thereof and R_3 is p-phenylene.

3. The lubricant composition of claim 1 in which R_1 and R_2 are alkylphenyl with alkyl groups of 8 to 24 carbon atoms and R_3 is m-phenylene.

4. The lubricant composition of claim 3 in which the detergent is an alkenyl succinimide.

5. The lubricant composition of claim 4 in which the detergent additive is a polybutenyl succinimide prepared from a polybutenyl succinic anhydride having about 65 carbon atoms in the alkenyl chain and tetraalkylene pentamine, said detergent additive being present in an amount from 0.1% to 10% by weight.

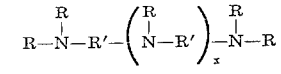
6. The lubricant composition of claim 5 wherein the inhibitor is isophthaloyl bis O,O-di(alkylphenyl) phosphorodithioate having an average of 13 alkyl carbons on each phenyl group.

7. The lubricant composition of claim 5 wherein the inhibitor is terephthaloyl bis O,O-dialkylphosphorodithioate in which the alkyl radicals comprise a mixture of isobutyl and amyl radicals.

8. The lubricant composition of claim 5 wherein the inhibitor is terephthaloyl bis O,O-dialkyl phosphorodithioate in which the alkyl radical comprises a mixture of isobutyl and hexyl radicals.

9. The lubricant composition of claim 1 in which the

detergent additive is an aliphatic hydrocarbon substituted polyamine of the formula:



in which R′ is an alkylene group of 1 to 8 carbon atoms, R is hydrogen or an aliphatic hydrocarbon radical of 425 to 50,000 molecular weight, x is an integer of 1 to 5 and at least one R is an aliphatic hydrocarbon radical.

10. The lubricant composition of claim 9 in which at least one R is derived from a polyolefin.

11. The lubricant composition of claim 10 in which at least one R is derived from polyisobutylene, R′ is ethylene and x is 4.

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