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AMINE SALTS OF DITHIOPHOSPHORIC ACIDS

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ABSTRACT OF THE DISCLOSURE

Lubricating oil additives having antiwear and detergent-inhibitor properties are prepared by P_2S_5 treating the reaction product of a high molecular weight carboxylic acid, e.g. polyisobutenyl propionic acid, with an amino-hydroxy compound, e.g. 2,2'-iminodiethanol, and neutralizing the thus produced dithiophosphoric acid with a mono or polyamine.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a lubricant additive composition which comprises amine derivatives of dithiophosphoric acid compounds. More particularly, the invention pertains to oil-soluble amine derivatives of dithiophosphoric acid compounds prepared from P_2S_5 treated hydroxy-containing amides produced by reacting a high molecular weight carboxylic acid with a hydroxy-containing amine. In another aspect, the invention is concerned with lubricant compositions containing small amounts of a dithiophosphoric acid neutralized with an amine wherein the dithiophosphoric acid is prepared by P_2S_5 treating a N-(hydroxy-containing hydrocarbyl) alkenyl-substituted monocarboxylic amide.

Description of the prior art

Lubricants for modern high compression piston type internal combustion engines are required to have high detergency, efficient sludge dispersing action and high oxidation resistance in order that those engines will be kept free of varnish, sludge and coke-like deposits. In other words, a heavy duty detergent type lubricating oil must be employed in such engines in order to maintain a high degree of engine cleanliness and thus promote engine life.

In the past, the majority of detergents, sludge dispersants and antioxidant materials that have been developed for use in lubricating oils for internal combustion engines have been metallic derivatives, particularly alkaline earth metal sulfonates, alkaline earth metal salts of alkyl phenol sulfides, colloidal dispersions of metallic carbonates (particularly alkaline earth metal carbonates), and the like. While, in general, additives of these types have proved to be quite satisfactory in their function as sludge dispersants and detergents, in many instances the ash content of these additives has presented a disadvantage in that the ash tends to accumulate in the combustion chamber of the engine to thereby cause preignition, spark plug fouling, valve burning and similar undesirable conditions. For this reason, an effective dispersant that is ashfree is preferable over an ash-forming detergent additive such as an alkaline earth metal salt of the types mentioned above. Ashfree dispersants are also of advantage in motor fuels, fuel oil compositions, and diesel fuels.

SUMMARY OF THE INVENTION

It has now been found, in accordance with the present invention, that certain amine derivatives of dithiophosphoric acid compounds function as effective ash-free antiwear and detergent-inhibitor additives in lubricating oils. Broadly, the additive of this invention is a dithophosphoric acid neutralized with a mono- or polyamine wherein the dithiophosphoric acid is prepared by P_2S_5 treating a N-(hydroxy - containing hydrocarbyl) alkenyl - substituted C_3–C_8 monocarboxylic amide. The hydrocarbyl referred to is a hydrocarbon radical selected from the group consisting of alkyl, cycloalkyl, aryl, and alkylaryl containing from 1 to 30 carbon atoms, preferably 1 to 12 carbon atoms. The hydrocarbyl may also include alkoxyalkyl, alkoxyaryl, iminoalkyl and iminoaryl C_1–C_{30} radicals, i.e., those radicals having the formula: $(R—X)_n$ R—X—R wherein X represents oxygen or nitrogen, *n* represents an integer ranging from 0 to about 10 and R represents an alkyl and/or aryl group of the type immediately following. Specific examples of hydrocarbyl groups include, among others, methyl, ethyl, butyl, hexyl, decyl, dodecyl, phenyl, tolyl, nphthyl, biphenyl, cyclohexyl, ethylcyclohexyl, cycloheptyl, methylcycloheptyl, ethoxyethyl, butoxybutyl, p-methoxyphenyl, etc. A preferred amide is N-(hydroxy-containing C_1–C_6 alkyl) alkenyl-substituted C_3–C_8 monocarboxylic amide. Even more preferred is N-di(hydroxy-containing C_1–C_6 alkyl) alkenyl-substituted C_3–C_8 monocarboxylic amide. The alkenyl group referred to is C_2–C_5 olefin polymerized to a molecular weight of 400–3000.

The N-(hydroxy-containing hydrocarbyl) alkenyl-substituted C_3–C_8 monocarboxylic amide is prepared by simple reaction between a hydroxy-containing amine and an alkenyl-substituted C_3–C_8 monocarboxylic acid under conditions of amide formation. Typically, the alkenyl group is a polymer of a C_2–C_5 monoolefin, e.g. polyethylene, polypropylene, polyisobutylene, polybutene, polyamylene, ethylene-propylene copolymer, propyleneisobutylene copolymer, etc., wherein the olefin polymer has a number average molecular weight within the range of from about 400 to about 3000. Especially useful products are obtained when the alkenyl group is polyisobutenyl having a molecular within the range between about 700 and 1200.

In general, the aforedescribed alkenyl-substituted C_3–C_8 monocarboxylic acid may be derived from an alpha-beta-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms and the aforedescribed C_2–C_5 mono-olefin polymer in accordance with well-known techniques. For example, the C_2–C_5 mono-olefin polymer may be halogenated with either bromine or chlorine, preferably the latter, using sufficient halogen to provide about one to two atoms per molecule of the olefin polymer. Halogenation can be effected at a temperature within the range from about ordinary ambient temperatures to about 250° F. To aid in the halogenation step, the polymer may be dissolved in a suitable solvent, such as carbon tetrachloride, although the use of such a solvent is not necessary. The time required for halogenation may be varied to some extent by the rate at which the halogen is introduced. Ordinarily from about 2 to about 5 hours is a satisfactory halogenation period. In a representative plant scale operation involving the chlorination of polyisobutylene of 830 molecular weight, a 100 pound batch will be chlorinated with 10 pounds of chlorine introduced into the reactor over a

period of 3½ hours with a chlorination temperature of about 250° F.

The halogenated polymer thus obtained is condensed with an alpha, beta-unsaturated, monocarboxylic acid of from 3 to 8 carbon atoms. Ordinarily, because of their greater availability, acids of this class having 3 or 4 carbon atoms will be used. Such acids include acrylic acid, alpha-methylacrylic acid (i.e. 2-methyl propenoic acid) and crotonic or isocrotonic acid (beta-methacrylic acid). Other alpha, beta-unsaturated acids that may be employed include tiglic acid (alpha, methylcrotonic acid), angelic acid (alpha-methylisocrotonic acid), sorbic acid, and cinnamic acid.

In an alternate preparation the halogenated polymer may be condensed with an ester of the C_3 to C_8 unsaturated monocarboxylic acid, e.g., ethyl methacrylate, in place of the free acid. The esters that may be used in this alternate preparation are those of aliphatic alcohols having from 1 to 10 carbon atoms, including methyl, ethyl, isopropyl, isobutyl, amyl, hexyl 2-ethyl hexyl decyl, and C_8 oxo alcohols. Such esters include amyl acrylate, isopropyl methacrylate, butyl crotonate, methyl acrylate, etc. In the subsequent amidation reaction an alcohol will be split out in place of water. The higher boiling the alcohol, the more difficult will be the removal of the alcohol from the reaction mixture. Generally, alcohols boiling above about 285° F. will not be desirable for this reason. Furthermore, use of higher boiling alcohols represents an economic disadvantage in that excess weights of materials are thus being put into the reaction only to be removed later. Most preferably, the esters that will be used here are those of C_1-C_5 aliphatic alcohols.

When the alkenyl substituted monocarboxylic acid is prepared by condensing the halogenated polyolefin with the alpha, beta-unsaturated acid or with an aliphatic ester thereof, at least one mole of acid or ester is used per mole of halogenated polyolefin. Normally, the acid or its ester will be employed in excess and may amount to as much as 1.5 to 2 moles per mole of halogenated polyolefin. The condensation temperature may be in the range of from about 300° to 500° F. and will more preferably be within the range of from about 375° to 475° F. The condensation temperature may require from about 3 to about 24 hours but will ordinarily take place in from 6 to 18 hours. After the reaction has been completed, excess acid or ester may be purged from the mixture, for example, by blowing with a stream of nitrogen at a temperature of 400° to 500° F.

The present invention is not known to be dependent in any way on the method of preparing the aforedescribed alkenyl-substituted carboxylic acid. Other methods for their preparation are well known to those skilled in the art. Consequently, such materials may be used regardless of their source.

The aforedescribed alkenyl-substituted monocarboxylic acid is reacted with a hydroxy-containing primary or secondary amine to produce an intermediate amide product which is subsequently P_2S_5 treated. As previously indicated, this intermediate product is a N-(hydroxy-containing hydrocarbyl) alkenyl-substituted monocarboxylic amide. Specific examples of suitable hydroxy containing primary amines include, among others, ethanolamine, propanolamine, 6-amino-1-hexanol, 5-amino-1-pentanol, aminocyclopentanols, aminocyclohexanols, o, m or p-aminophenols, aminonaphthols, 2-(2-aminoethoxy) ethanol, 2-(2 iminoethylamino) ethanol, etc. Non-limiting examples of suitably employed monohydroxy or dihydroxy secondary amines (i.e. monohydroxy or dihydroxy-containing imino compounds) include 2,2'-iminodiethanol; 1,1'-iminodi-2-isopropanol; N,N-bis (4-cyclohexanol) amine; and 4,4'-dihydroxydiphenylamine.

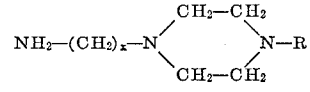
The alkenyl-substituted carboxylic acid and hydroxy-containing amine compounds are reacted under conditions causing amide formation. Such conditions are well known in the art, and it is not intended that the additive of this invention be limited to any specific method of preparation. By way of example, the amide can be formed by reacting the carboxylic acid and the hydroxy-containing amine compound in the presence of a suitable solvent, e.g. neutral mineral oils, toluene, xylene, etc., at elevated temperatures, e.g. 230° F.–450° F., and atmospheric pressure for a period of time ranging from about 4 to about 24 hours.

The aforedescribed N-(hydroxy-containing hydrocarbyl) alkenyl-substituted amide is reacted with a phosphorus sulfide such as phosphorus pentasulfide, P_2S_5, under conditions causing phosphorodithioic acid formation. The dithiophosphoric acid formation is effected by means well known in the art. For example, the P_2S_5 may be reacted with a single hydroxy-containing amide compound or mixtures of said compounds by mixing the reactants at a temperature of about 125° to 175° C., preferably 140° to 160° C. using about 0.25 to about 0.50 moles of P_2S_5 per alcohol group. The completion of the reaction may be noted visually and will be indicated by the dissolution of the P_2S_5. The reaction time required would generally be in the range of about 0.5 to 24 hours, usually about 3 to 6 hours. After the reaction is completed, the reaction is preferably blown with nitrogen or other inert gas to remove hydrogen sulfide therefrom. If desired, the reaction may be carried out in a solvent such as a mineral oil, toluene, xylene, etc.

The dithiophosphoric acid thus formed is neutralized with acyclic or cyclic, primary and secondary mono and poly amines containing from 1 to about 24 carbon atoms. It is preferred, however, to use an aliphatic polyamine having the following general formula:

$$NH_2(CH_2)_n\text{—}\left[NH(CH_2)_n\right]_m\text{—}NH_2$$

wherein n is 2 to 3 and m is a number from 0 to 10. Specific compounds coming within the formula include, among others, diethylene-triamine, tetraethylenepentamine, dipropylenetriamine, octaethylenenonamine, and tetrapropylenepentamine, N,N-di(2-amino-ethyl) ethylenediamine may also be used. Other aliphatic polyamino compounds that may be used are N-aminoalkyl-piperazines of the formula:



wherein X is a number 1 to 3, and R is hydrogen or an aminoalkyl radical containing 1 to 3 carbon atoms. Specific examples include N-(2-aminoethyl) piperazine, N-(2-aminoisopropyl) piperazine, and N,N'-di-(2-aminoethyl) piperazine.

The use of mixtures of alkylene polyamines, mixtures of N-aminoalkyl piperazines, and mixtures of the alkylene polyamines with the N-aminoalkyl piperazines is also contemplated, and the term aliphatic polyamine is intended to embrace all of these materials.

Neutralization of the dithiophosphoric acid with the amine is conventionally effected, for example, by simple mixing of the reactants at ambient temperatures and pressures.

The additive products of this invention may be incorporated in lubricating oil compositions in concentration ranges of from about 0.001 to about 10 wt. percent and will ordinarily be used in concentrations of from about 0.1 to about 5 wt. percent. The lubricating oils to which the additives of the invention may be added include not only mineral lubricating oils, but synthetic oils also. The mineral lubricating oils may be of any preferred types, including those derived from the ordinary paraffinic, naphthenic, asphaltic, or mixed base mineral crude oils by suitable refining methods. Generally they will have a viscosity of 210° F. of between about 45 and about 90 SUS (Saybolt Universal Seconds) and at 100° F. a viscosity of between about 150 and about 1,100 SUS. The viscosity

indices of these oils will generally range between about 0 and about 100 or more. In the case of oils employed in high speed, heavy duty Diesel engines, oils of high viscosity indices are often preferred, i.e. of the order of 100 or higher, but usually most Diesel engines employ lubricating oils having viscosities of between about 75 and about 80 SUS at 210° F. and at 100° F. of between about 800 and about 1,250 SUS with viscosity indices ranging between about 55 and about 80. Synthetic hydrocarbon lubricating oils may also be employed. These synthetic oils include, among others, dibasic acid esters such as di-2-ethyl hexyl sebacate, carbonate esters, phosphate esters, halogenated hydrocarbons, polysilicones, polyglycols, glycol esters such as C_{13} oxo acid diesters of tetraethylene glycol, and complex esters as for example the complex ester formed by the reaction of 1 mole of sebacic acid with 2 moles of tetraethylene glycol and 2 moles of 2-ethyl hexanoic acid.

In the lubricant compositions of this invention, other conventional additives may also be present, including dyes, pour point depressants, antiwear agents, e.g. tricresyl phosphate, zinc dialkyl dithiophosphates of 3 to 8 carbon atoms, antioxidants such as phenyl-alpha-naphthylamine, tertiary octylphenol sulfide, bis-phenols such as 4,4'-methylene bis 2,6-ditertiary butylphenol), viscosity index improvers such as polymethacrylates, polyisobutylene, alkyl fumarate-vinyl acetate copolymers, and the like, as well as other dispersants.

It is within the contemplation of this invention to prepare additive concentrates in which the concentration of additive is greater than would normally be employed in a finished lubricant. These concentrates may contain in the range of from 10 to 80% of additive on an active ingredient basis, the balance being a hydrocarbon solvent such as, for example, a mineral oil. Such concentrates are convenient for handling the additive in the ultimate blending operation into a finished lubricating oil composition. The additive concentrates may be made up simply of an additive of the persent invention in a suitable mineral oil medium or they may include other additives that are intended for use along with the additives of the invention in a finished lubricant. Thus, if the additives are to be used in conjunction with conventional detergents, an additive concentrate can be prepared containing say 30 to 60 wt. percent of an additive of the invention and 5 to 20 wt. percent of a metal sulfonate, e.g. calcium petroleum sulfonate from sulfonic acids of about 450 molecular weight, or a metal alkylphenol sulfide, e.g. calcium nonylphenol sulfide, with the balance being a mineral lubricating oil. Additionally, 5 to 15 wt. percent of an antiwear agent such as zinc dialkyldithiophosphate, e.g. mixed zinc butyl and amyl dithiophosphates may also be present in the additive concentrate package.

The invention can be more fully understood by reference to the following examples.

EXAMPLE 1

This example serves to illustrate the preparation of a polyisobutenyl propionic acid.

A 110-pound portion of polyisobutylene of 780 molecular weight (as determined by osmometry) was heated to 250° F., then a stream of chlorine was passed through the heated polyisobutylene at the 250° F. temperature at a rate of 2.5 pounds of chlorine per hour for a total of 4 hours, the total chlorine treat thus being 10 pounds. A sample of the chlorinated product analyzed 4.3% chlorine and had an API gravity of 23.3. To the chlorinated polyisobutylene there was added 10.5 pounds of acrylic acid. Over a period of two hours the temperature was raised from 250° F. to 425° F. and the pressure was increased to 20 p.s.i.g. Heating was continued for 5 hours at 425° F. and the reaction vessel was vented to maintain the pressure of 20 p.s.i.g. The pressure was then released and the mixture was purged with nitrogen for 2 hours to remove unreacted acrylic acid. The polyisobutenyl propionic acid thereby obtained weighed 109.3 pounds and had a total neutralization number (ASTM D–664) of 46.2 milligrams of KOH per gram. The chlorine content was found to be 0.3 wt. percent.

EXAMPLE 2

An additive of this invention was prepared as follows: Into a glass reaction vessel fitted with a mechanical stirrer, heating mantle, thermometer and condenser containing 1,245 grams of polyisobutenyl propionic acid produced in the manner of Example 1 (number average molecular weight 1245, ASTM Neut. No. 45) in 1,000 grams of a solvent neutral mineral oil (150 SUS viscosity at 100° F.) there were charged 105 grams of 2,2'-iminodiethanol. The resulting mixture was then heated at about 300° F. for a period of about 16–18 hours. The reaction mixture was thereafter cooled to about 150° F. whereupon 111 grams of P_2S_5 was added over a period of about 15 minutes. Upon completion of the P_2S_5 addition, the mixture was heated at about 300° F. for about 4 hours. The mixture was then cooled to room temperature and 52.5 grams of diethylene triamine was slowly added over a period of about 30 minutes. After stirring for 1 hour, the product was filtered through Dicalite in the cold. The final product recovered totaled 2322 grams of which 55 wt. percent was additive product, the remainder being the mineral oil.

EXAMPLE 3

The procedure of Example 2 is repeated, but instead of the iminodiethanol the polyisobutenyl propionic acid is reacted with 61 grams of ethanol amine. The resulting hydroxy-containing amide product is then treated with 55.5 grams P_2S_5 and thereafter reacted with the diethylenetriamine.

A number of routine tests were carried out on a typical base oil containing the novel additive hereinbefore described in order to illustrate the beneficial effects derived therefrom. The following tests were performed:

(1) An Oxidation Stability Test was used for a laboratory evaluation of the antioxidant properties of the additive. This test involves heating the compounded oil to a temperature of about 340° F. in the presence of a copper-lead oxidation catalyst while intimately mixing the compounded oil with air at the rate of 2 c.f./hr. The viscosity increase (SUS, at 100° F.) after 23 hours is measured and a determination of the percentage of viscosity increase over that of the original unoxidized oil is made.

(2) A Copper-Lead Bearing Weight Loss, in milligrams, involving the compounded oil was also conducted. The measure of the change in weight of the Cu-Pb catalyst in test (1) in milligrams is determined.

(3) The well-known Falex Test as described in, for example, U.S. Steel Manual, Proposed Falex Machine Method ASTM D–2 Section V, Tech. k was used to determine the antiwear properties of the novel additives.

(4) The Disc and Rider Test was also used to evaluate the antiwear properties of the additives. In this test, a spinning (50 r.p.m.) steel disc is contacted with a fixed steel ball (1.25 cm. dia.), and a load of 500 g. is then impressed upon the disc. A film of oil is maintained on the spinning disc at the point of contact with the steel ball. A constant electrical voltage is then applied between the spinning disc and the steel ball. The resulting resistance is measured after 20 minutes for tests employing the base oil with no additive and the base oil containing an additive of this invention. The resistance recorded when employing the base oil alone was given a metallic contact of 100%, and other resistance readings were given proportionately higher or lower percent metallic contact, i.e. the resistance between the ball and disc was found to be proportional to the percent metallic contact with the higher percent metallic contact giving the lower resistance.

A series of tests were carried out using a typical base oil containing various amounts of additive of this invention and prior art additives. The base oil can best be described as being a phenol extracted oil having a viscosity at 210° F. of 60 SUS and at 100° F. of 460 SUS. The results are given below in Tables I–III.

TABLE I.—OXIDATION STABILITY TEST

Oil tested	Percent viscosity increase SUS	Cu-Pb bearing weight, loss, mg.
Base oil alone	85	143
Base oil plus 5.0 wt. percent of product of Example 2 (55 wt. percent active ingredient)	8.6	27
Base oil plus 5.5 wt. percent of PIBA/TEPA concentrate [2]	110	330
Base oil plus 5.0 wt. percent of PIBA/TEPA condensate [2] plus 0.5 wt. percent Ethyl 728 [3]	85	223
Base oil plus 3 wt. percent of PIBA/TEPA condensate [2] plus 0.5 wt. percent Ethyl 728 [3] plus 2.0 wt percent of product of Example 2	7.2	28

[1] At 100° F., 23 hours.
[2] Condensation product of 3 parts by weight of polyisobutenyl propionic acid (830 mol. wt.) and 1 part by weight of tetraethylenepentamine (50 percent A.I.).
[3] Bisphenol antioxidant.

From the above data in Table I, it is readily apparent that the amine neutralized dithiophosphoric acid of this invention is very effective in providing oxidaton stablity and inhibition of Cu-Pb corrosion.

TABLE II

Falex text [1]

Oil tested:	Mg. wt. loss
Base oil alone	Failure
Base oil plus 2.0 wt. percent of Product of Example 2 (55 wt. percent active ingredient)	1.1

[1] 2 min. @ 250 lb. 8 min. @ 400 lb.

TABLE III.—DISC AND RIDER TEST

Oil tested	Coefficient of friction, μ avg.	Percent metallic contact
Base oil alone	0.148	100
Base oil plus 1.0 wt. percent of product of Example 2 (55 wt. percent active ingredient)	0.116	65

It is seen from the data presented in Tables II and III that the additive of this invention is an effective antiwear agent.

What is claimed is:

1. An amine neutralized derivative of a dithiophosphoric acid prepared by reacting an alkenyl-substituted C_3–C_8 monocarboxylic acid, wherein the alkenyl group is a polymerized C_2–C_5 monoolefin having a molecular weight between about 400 and about 3000 with a primary or secondary hydroxy-containing amine selected from the group consisting of mono and di C_1–C_6 alkylol amine, mono and diphenylol amine, mono cyclopentanol amine, mono and dicyclohexanol amine, to form the corresponding N - (hydroxy-hydrocarbon) substituted amide, reacting the said amide with phosphorus pentasulfide and neutralizing the resultant dithiophosphoric acid with a polyamine having the formula:

$$NH_2(CH_2)_n—[NH(CH_2)_n]_m—NH_2$$

wherein n is 2 to 3 and m is a number from 0 to 10.

2. An amine neutralized derivative of a dithiophosphoric acid as in claim 1 wherein the hydroxy-containing amine is a C_1–C_6 alkylol amine.

3. An amine neutralized derivative of a dithiophosphoric acid as in claim 2 wherein the hydroxy-containing amine is diethylol amine.

4. An amine neutralized derivative of a dithiophosphoric acid as in claim 1 wherein the alkenyl group has a molecular weight of between about 700 and about 1200.

5. An amine neutralized derivative of a dithiophosphoric acid as in claim 4 wherein the alkenyl group is polyisobutenyl of about 780 molecular weight and the monocarboxylic acid is propionic acid.

6. An amine nuetralized derivative of a dithiophosphoric acid as in claim 5 wherein the neutralizing polyamine is diethylene triamine.

7. An amine neutralized derivative of a dithiophosphoric acid as in claim 6 wherein the hydroxy-containing amine is diethylol amine.

No references cited.

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