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REACTION PRODUCTS OF AMINES AND DITHIOPHOSPHORIC ACIDS OR SALTS

Alfred Goldschmidt, El Cerrito, Calif., assignor to Chevron Research Company, San Francisco, Calif.

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ABSTRACT OF THE DISCLOSURE

Novel compositions useful as lubricating oil additives are produced by reacting an amine and a dithiophosphoric acid or salt at a temperature of 140°–200° C.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to additives for automotive engine lubricating oils.

Automotive engine lubricants commonly contain additives designed to reduce the oxidation of the oil at the high temperatures encountered in engines. Many lubricating oils also contain antiwear or extreme pressure ("EP") additives to provide lubrication under boundary lubrication conditions. A large number of additives of both types are known.

Description of the prior art

U.S. Pat. 2,737,492 discloses an "alkaline reserve improvement agent." This is a metal-containing complex in which the nitrogen atoms of one or more ammonia or monoamine molecules are coordinated with the metal atom of a metallic salt of an O,O-diester of dithiophosphoric acid. The number of ammonia or monoamine molecules coordinated with the metal will generally be twice the valence number of the metal. The reaction to form the metallic complex is conducted at ambient temperature (~25° C.). A similar metal complex is disclosed in U.S. Pat. 3,284,354. This metal complex is formed at ambient temperature by the coordination of a polyamine containing 2 to 12 amino groups with the metal atom of a metal salt of an O,O-diester of dithiophosphoric acid. U.S. Pat. 3,103,492 describes the formation at ambient temperature of a complex of a monoamine and an O,O-dialiphatic ester of dithiophosphoric acid. U.S. Pat. 3,361,668 describes the formation of improved O,O'-diester of phosphorodithioic acid by the reaction at 20°–200° C. of one mole of phosphorous pentasulfide with four equivalents of a mixture of alcohols or phenols and monoamines. The alcohol-phenol/moonamine mixture contains 95–99.95 weight percent alcohol or phenol and 0.05 to 5 weight percent monoamine. The diester may be prepared by reaction of the phosphorous pentasulfide and the alcohol or phenol and then a small amount of monoamine added.

SUMMARY

I have now discovered a novel composition useful as a lubricating oil additive that provides both antiwear and antioxidation properties to the oil. This composition is prepared by reacting at 140° C. to 200° C., (1) a C_1–C_{50}, N_1–N_6 aliphatic hydrocarbon amine in which the nitrogen atoms are present in primary or secondary amino groups;

and (2) an O,O-di(C_{18}–C_{50} hydrocarbyl) dithiophosphoric acid or salt; in a ratio of not greater than one mole of amine per equivalent of dihydrocarbyl dithiophosphoric acid. This invention also includes a lubricating composition comprising a major portion of a hydrocarbon oil of lubricating viscosity and a minor amount of this additive.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of this invention are novel materials useful as combined antioxidation and EP additives for automotive engine lubricants. Lubricating oils containing these additives show significantly greater oxidation inhibition in the "Oxidator B" test than do prior art lubricants containing mixtures of alkenyl succinimides and zinc dialkaryl dithiophosphates. Lubricants containing these additives also cause significantly less copper corrosion in the L–38 Strip Test than do similar oils containing zinc dialkaryl dithiophosphates alone. In the Falex Test, oils containing these additives and alkenyl succinimides have been found to have better load-carrying capacities than oils containing either succinimides alone or mixtures of succinimides and zinc dialkaryl dithiophosphates.

The compositions of this invention are mixtures of compounds containing only carbon, hydrogen, oxygen, phosphorus, sulfur and nitrogen. Of the nitrogen present, usually 20 to 30 percent will be basic nitrogen, although basic nitrogen can be as high as about 60–70 percent. All the sulfur and a portion of the nitrogen in the product will be bonded directly to the phosphorus. The sulfur content will be reduced, usually by half, from the sulfur content of the reactants. When one reactant is the dithiophosphoric acid, the reaction product contains hydrogen sulfide mixed with the novel composition; when one reactant is the salt, the reaction product will contain a peptized metal sulfide along with this composition.

The compositions of this invention are produced by reacting at temperatures in the range of 140° C. to 200° C., (1) an aliphatic hydrocarbon amine of from 1 to 6 nitrogen atoms and 1 to 50 carbon atoms per molecule, in which the nitrogen atoms are disposed solely in primary or secondary amino groups, and (2) an O,O-dihydrocarbyl dithiophosphoric acid or salt wherein each hydrocarbyl radical in the molecule is of from 18 to 50 carbon atoms. The ratio of the reactant amine to the reactant O,O-dihydrocarbyl dithiophosphoric acid or salt is in the range of 0.1–1:1, usually 0.25–0.50:1, moles of amine per equivalent of acid or salt.

One of the two reactants used to form the compositions of this invention is a saturated aliphatic hydrocarbon amine having from 1 to 50 carbon atoms and 1 to 6 nitrogen atoms per molecule. Usually there will be 2 to 12 carbon atoms and 2 to 5 nitrogen atoms, preferably 2 to 6 carbon atoms and 2 to 3 nitrogen atoms, per molecule. The aliphatic hydrocarbon portion of the molecule may be straight- or branched-chain, usually srtaight-chain.

The nitrogen atoms in the molecule will usually be in the form of primary or secondary amino groups. Both primary and secondary amino groups may be present in a single molecule. Where the compound is a monoamine, it will usually have a primary amino group, which is preferably located at a terminal position in the molecule. Where the compound is a polyamine, it may have a mixture of primary and secondary amino groups. Usually the primary amino groups are attached to each terminal car-

bon atom in the molecule. The compounds most commonly used are thus the 1-amino hydrocarbons and the polyamines having alpha and omega amino groups.

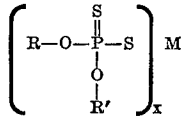
The preferred amines are the polyamines. The compositions derived from them show better antioxidation character than the compositions derived from monoamines.

Typical monoamines which may be used include aminomethane, 1-aminoethane, 1-amino-*n*-butane, 1-amino-*n*-hexane, 1-amino-*n*-decane, 1-amino-*n*-dodecane, 1-amino-*n*-pentadecane, 1-amino-*n*-triacontane, 1-amino-*n*-pentacontane, 1-amino-3-methylpentane, 1-amino-3,5-dimethyldecane, 3-aminopentane, 3-amino-3-methylpentane, ethylaminoethane, ethylaminopropane, methylaminopentane, propylaminopropane, butylaminooctane, etc.

Typical polyamines which are suitable for use in this invention include ethylene diamine, diethylene triamine, triethylene pentamine, tetraethylene pentamine, pentaethylene hexamine, propylene diamine, dipropylene triamine, hexamethylene diamine, 2,2'-diaminodiethylamine, 3,3'-diaminodipropylamine, 2,4-diaminopentane, 2,9-diaminodecane, bis(ethylamino)ethane, 2,8-diamino-4-octene, etc.

One may also use compounds formed by reacting a monoamine or polyamine with a hydrocarbon polymer of from 4 to 49 carbon atoms. The total number of carbon atoms in the entire molecule will not exceed 50. The hydrocarbon polymers are prepared by polymerizing low molecular weight olefins such as ethylene, propylene, or isobutylene.

The other principal reactant used to prepare the compositions of this invention is a dihydrocarbyl dithiophosphoric acid or a salt of such an acid. The dihydrocarbyl dithiophosphoric acids or salts have the following formula:



wherein R and R' are each hydrocarbon (or "hydrocarbyl") of from 18 to 50 carbon atoms, M is hydrogen or a divalent metal atom, and x is 1 when M is hydrogen and 2 when M is a divalent metal. "Hydrocarbyl" as used herein refers to structures containing only hydrogen and carbon atoms. The hydrocarbyl radicals are usually alkaryl radicals of 18 to 30 carbon atoms each. The alkyl portion of each radical should contain a linear portion of at least 8 carbon atoms bonded to the benzene ring. If desired, alkyl radicals may be substituted for either or both alkaryl radicals, but each alkyl radical must contain at least 24 carbon atoms to prevent precipitation in the reaction product.

Typical alkaryl or alkyl radicals which may constitute the hydrocarbyl portion of the O,O-dihydrocarbyl dithiophosphoric acid include 4-*n*-dodecylphenyl, 4-*n*-octadecylphenyl, 3 - *n*-octadecylphenyl - 4-(1'-methylpentadecyl) phenyl, 4-(1',3',5',7'-tetramethyloctyl)phenyl, 4-(1',3',5',7',9',11' - hexamethyhexadecyl)phenyl, *n*-octadecyl, *n*-tetracosyl, *n*-triacontyl, *n*-tetracontyl, *n*-pentacontyl, 6,12-dimethyldocosyl, and the like.

M, when a metal, may be any divalent metal of Group II–A or II–B of the Periodic Table. Usually, the metal will be calcium, barium, or zinc. Of these, zinc is preferred.

The reaction to produce the compounds of this invention is conducted at a temperature of 140° C. to 200° C., usually 150° C. to 185° C. The reaction may be conducted in a solvent. The solvent may be any neutral medium in which the reactants and product are soluble, either neat or with suitable emulsifiers. It is preferred that the solvent be a hydrocarbon solvent and, preferably, an alkyl aromatic hydrocarbon solvent with a suitable boiling point. Typical alkyl aromatic hydrocarbon solvents are toluene, and the mixed xylenes. The reaction will be conducted for a period of from 1 to 12 hours, preferably 2 to 6 hours.

The ratio of the hydrocarbon amine to the dihydrocarbyl dithiophosphoric acid or salt will be in the range of 0.1 to 1.0 moles of amine per equivalent of acid or salt. It is preferred that the ratio be in the range of 0.25 to 0.5 moles of amine per equivalent of salt or acid. When amine is used in excess, an undesirable precipitate is formed.

The course of the reaction and the degree of completion can be determined from infrared analysis of the reaction mixture. The amine will react with the acid or salt to yield a new product containing a smaller amount of ester groups. Since the P—O—$C_{aromatic}$ bonds produce an absorption peak at 11μ in the infrared spectrum, the course of the reaction may be followed by observing the decrease in the size of this peak. Degree of completion of the reaction will be indicated by proportionate reduction of the peak height.

The compositions of this invention may be used as additives in a wide variety of lubricating oils. These are lubricating fluids derived from natural or synthetic sources, and having viscosities from about 35 to 50,000 SUS at 100° F. These include the natural hydrocarbonaceous oils which may be paraffin-base, naphthenic-base, asphaltic-base, or mixed-base oils; synthetic hydrocarbon oils such as polymers of the C_2–C_8 olefins and alkylated aromatic hydrocarbons; and synthetic nonhydrocarbon oils such as polyalkylene oxides, aromatic ethers, carboxylate esters, phosphate esters, and silicon esters. The preferred lubricating oils are the hydrocarbonaceous oils, both natural and synthetic. The above oils may be used individually or together whenever miscible or made so by the use of mutual solvents. The lubricants of this invention will normally contain at least 85 weight percent of the lubricating oil. The additives of this invention may, as noted below, be put into concentrates, often for convenience in shipping, which contain 30–85 weight oil. These concentrates may also contain other additives, and are diluted with additional oil prior to use.

The compositions of this invention will be present in the overall lubricating composition in a concentration of from 0.1 to 5.0 weight percent, preferably, 1.0 to 3.0 weight percent. In concentrates, these compositions may be present in an amount of from 5 to 70 weight percent.

Other additives may also be included in the lubricants, such as pour point depressants, oiliness agents, rust inhibitors, detergents, etc. For oils to be used in an engine, the total amount of these additives will generally be in the range of from 0.1 to 10 weight percent, more usually from about 0.5 to 5 weight percent. The individual additives may vary in amounts from about 0.01 to 5 weight percent in the total composition. In concentrates, the weight percent of these additives will usually range from about 0.3 to 50.

The following examples will illustrate the compositions of this invention:

EXAMPLE A

A zinc O,O-dihydrocarbyl dithiophosphate was prepared by conventional methods. The ester groups were derived from a mixture of alkylated phenols which had been alkylated by propylene polymers having an average total of 12–14 carbon atoms and a linear chain of about 8 carbon atoms per molecule. Each hydrocarbon radical in the acid molecule, therefore, contained 18–20 carbon atoms. The salt was then dispersed in a hydrocarbon lubricating oil. This oil solution contained approximately 2.85 weight percent phosphorus, 3.15 weight percent zinc, and 5.93 weight percent sulfur, and had a specific gravity of 12.1° API and a viscosity at 100° F. of 3,900 SUS. (This solution will hereinafter be referred to as "Salt A," for brevity.)

EXAMPLE B

An O,O-dihydrocarbyl dithiophosphoric acid was prepared by conventional methods from the same alkylated phenols as described above in Example A, and was dispersed in a hydrocarbon oil. This oil solution containing 3.1 weight percent phosphorus, 6.0 weight percent sulfur, and had a specific gravity of about 1. (This solution will hereinafter be referred to as "Acid B," for brevity.)

In the following examples, two alkyl aromatic solvents are mentioned. The first ("Solvent A") had an ASTM D–86 distillation range of 350°–415° F. and an ASTM D–611 mixed aniline point of about 65° F. The second ("Solvent B") had an ASTM D–86 distillation range of about 400°–500° F.

EXAMPLE 1

105 gm. (0.05 mole) of Salt A, 7.3 gm. (0.10 mole) of 1-aminobutane, and 100 ml. of Solvent A were mixed and heated at 180° C. for 6.3 hours. A 20 percent reduction in the 11μ infrared absorbence peak was observed. The product was found to have 1.00 weight percent nitrogen, and 5.54 weight percent sulfur.

EXAMPLE 2

64.5 gm. (0.03 mole) of Salt A, 6.06 gm. (0.06 mole) of 1-aminohexane, and 100 ml. of Solvent A were blended and heated at 180° C. for 6 hours. A 45 percent reduction in the 11μ absorbence peak was observed.

EXAMPLE 3

150 gm. (0.075 mole) of Salt A, 4.45 gm. (0.075 mole) of ethylene diamine, and 100 ml. of xylene were blended and heated at 150° C. for 12 hours. A 46 percent reduction in the 11μ peak was observed. The product contained 1.61 weight percent nitrogen, including 0.64 weight percent basic nitrogen.

EXAMPLE 4

100 gm. (0.05 mole) of Salt A, 3 gm. (0.05 mole) of ethylene diamine, and 100 ml. of Solvent A were blended and heated at 180° C. for 6 hours. The product contained 1.28 weight percent nitrogen, including 0.61 weight percent basic nitrogen.

EXAMPLE 5

1,050 gm. (1 mole) of Acid B, 32 gm. (0.5 mole) of ethylene diamine, and 200 ml. of Solvent A were stirred at 150° C. for 6 hours. A 49 percent reduction in the 11μ peak was observed. The product contained 1.52 weight percent nitrogen, including 0.7 weight percent basic nitrogen.

EXAMPLE 6

105 gm. (0.05 mole) of Salt A, 10.3 gm. (0.1 mole) of diethylene triamine, and 130 ml. of kerosene were heated at 180° C. for 6 hours. The product contained 1.91 weight percent nitrogen and 1.73 weight percent sulfur.

EXAMPLE 7

105 gm. (0.05 mole) of Salt A, 5.1 gm. (0.05 mole) of diethylene triamine, and 100 ml. of Solvent B were blended and heated at 180° C. for 6 hours. A 49 percent reduction in the 11μ absorbence peak was observed. The product contained 2.01 weight percent nitrogen, 2.8 weight percent phosphorus, and 4.96 weight percent sulfur.

EXAMPLE 8

158 gm. (0.15 mole) of Acid B, 7.6 gm. (0.075 mole) of diethylene triamine and 100 ml. of Solvent A were blended and heated at 180° C. for 6 hours. A 44 percent reduction in the 11μ absorbence peak was observed. The product contained 0.78 weight percent basic nitrogen, and 1.95 weight percent sulfur.

EXAMPLE 9

157 gm. (0.15 mole) of Acid B, and 7.6 gm. (0.075 mole) of diethylene triamine were blended and heated at 185° C. for 5 hours. No solvent other than the oil in Acid B was used. A 49 percent reduction in the 11μ absorbence peak was observed. The product contained 2.13 weight percent nitrogen, including 0.37 weight percent basic nitrogen, 3.0 weight percent phosphorus, and 3.15 weight percent sulfur.

EXAMPLE 10

500 gm. (0.49 mole) of Acid B, 25 gm. (0.24 mole) of diethylene triamine, and 100 ml. of Solvent A were blended and heated at 180° C. for 3 hours. A 47 percent reduction in the 11μ absorbence peak was observed. The product contained 1.90 weight percent nitrogen, 2.8 weight percent phosphorus, and 4.46 weight percent sulfur.

EXAMPLE 11

150 gm. (0.075 mole) of Salt A, 14.2 gm. (0.075 mole) of tetraethylene pentamine, and 100 ml. of Solvent A were blended and heated at 180° C. for 6 hours. The product contained 2.61 weight percent nitrogen, including 1.44 weight percent basic nitrogen.

EXAMPLE 12

150 gm. (0.075 mole) of Salt A, 9.5 gm. (0.05 mole) of tetraethylene pentamine and 100 ml. of Solvent A were blended and heated at 180° C. for 6 hours. A 50 percent reduction in the 11μ absorbence peak was observed. The product contained 2.20 weight percent nitrogen, including 0.85 weight percent basic nitrogen.

EXAMPLE 13

150 gm. (0.075 mole) of Salt A, 10 gm. (0.075 mole) of 3,3'-di(aminopropyl)amine and 100 ml. of Solvent A were blended and heated at 180° C. for 6 hours. The product contained 1.55 weight percent nitrogen, including 0.52 weight basic nitrogen.

EXAMPLE 14

56 gm. (0.03 mole) of Salt A, 41.5 gm. (0.06 mole) of a polyamine produced by reacting diethylene triamine with an isobutene polymer having a number average molecular weight of approximately 550, and 120 ml. of Solvent A were blended and heated at 180° C. for 6 hours. The product contained 2.10 weight percent nitrogen, including 0.90 weight percent basic nitrogen.

EXAMPLE 15

690 gm. (0.3 mole) of Salt A, 31 gm. (0.3 mole) of diethylene triamine, and 400 cc. of Solvent A were blended and heated at 180° C. for 5 hours.

EXAMPLE 16

The preparation of Example 15 was repeated four times to prepare a large quantity of material. The four samples were combined and the mixture used in tests described below.

A number of tests were used to evaluate the compositions of this invention. The first test was an oxidation test, designed to indicate the degree of oxidation inhibition provided to an oil by the claimed additives. Each test sample contained 95.7 weight percent of a hydrocarbon lubricating oil having a viscosity at 100° F. of approximately 480 SUS, and 4.3 weight percent of the particular test additive. Oil stability in the test was measured by the time required for the consumption of 1 liter of oxygen by 100 gm. of the test oil at 340° F. The actual test was run with a 25 gm. sample of oil and the results corrected to a 100 gm. sample. The oil was heated in the presence of an oxidizing catalyst (1.38 cc. per 100 cc. oil) containing a mixture of soluble salts providing 95 p.p.m. copper, 80 p.p.m. iron, 4.8 p.p.m. manganese, 1,100 p.p.m. lead, and 49 p.p.m. tin. The results of this test are summarized in Table I, below.

TABLE I

Additive:	Hours to absorb 1 liter of O_2
Salt A	[1] 6.3
Acid B	6.5
Composition of:	
Example 1	10.9
Example 2	9.8
Example 3	10.1
Example 4	9.4
Example 5	9.0
Example 6	11.4
Example 9	10.9
Example 11	8.5
Example 12	9.5
Example 13	10.1
Example 16	10.1

[1] Average of a plurality of tests.

It is apparent from the above data that the compositions of this invention provide good oxidation inhibition and provide substantially better oxidation inhibition than either a dithiophosphoric acid or a zinc dithiophosphate alone.

The compositions were evaluated for EP properties in the well-known "Falex Machine" test. This test is described by Faville et al. in *Lubrication Engineering* (August 1968), pp. 349–358. The Falex machine contained two steel V-blocks with a steel shaft rotating between them. The shaft was connected to the rotating head of the machine by a brass shear pin. In the test, the steel blocks and shaft were immersed in the test oil. The blocks were then forced against the shaft under increasing loads until seizure occurred. The load at seizure was recorded and reported as the test results.

The results of the Falex machine test of the compositions of this invention are reported in Table II below. The test oil base was a mid-Continent SAE 30 hydrocarbon oil containing 3.5 weight percent of a polyisobutenylsuccinimide produced by reacting tetraethylenepentamine, maleic anhydride, and a mixture of isobutene polymers having an average molecular weight of approximately 930. The test additive was added to this base in an amount sufficient to produce a concentration of 24 meq. of phosphorus per gallon of oil.

TABLE II

Additive:	Load at failure, lbs.
None (base only)	970
Zinc salt of di(C_{22}-alkylphenyl)-dithiophosphoric acid	1,430
Di(C_{22}-alkylphenyl)-dithiophosphoric acid	1,600
Composition of:	
Example 2	2,190
Example 3	1,340
Example 8	1,590
Example 15	1,270

It is apparent from these data that the compositions of this invention show EP properties as additives comparable to or better than those of known zinc dithiophosphates or dithiophosphoric acids. These materials also improve the load-carrying capacity of the base oil alone.

The anti-corrosion properties of the compositions of this inventoin were illustrated by their performance in the CRC L–38 Bearing Corrosion Test. In this test, separate strips of copper and lead were immersed in the test lubricant and the lubricant was heated for 20 hours at a temperature of 295° F. The copper strip was weighed and then washed with potassium cyanide solution to remove copper compound deposits. It was then reweighed.

The weight losses of the two strips were reported as a measure of the degree of corrosion caused by the oil.

The test samples in these experiments contained 1.3 weight percent of the test additive and 98.7 weight percent of a base oil consisting of 98 percent of the mid-Continent SAE 30 oil described above and 2.0 weight percent of the succinimide described above. The results of these tests are described in Table III below:

TABLE III

	Metal weight loss, mg.		
	Copper		
Additive	Before KCN	After KCN	Lead
Salt A	42.1	108.6	2.5
Composition of Example—			
8	6.4	38.2	1.7
16	14.1	43.9	3.6

It is apparent from these data that the compositions of this invention are substantially less corrosive to copper than are the conventional zinc dithiophosphates. It is also evident that they are equivalent to the zinc dithiophosphates in their negligible corrosive effect on lead.

The compositions of this invention also enhance the dispersant properties of detergent-containing lubricating oils. This is illustrated in Table IV, below, which presents the results of a pyruvic acid suspension test. In this test, 15 gm. of the test oil was weighed into an 8 dram vial. 1½ gm. of pyruvic acid was added, and the mixture was shaken gently for 24 hours. It was then centrifuged at 1,800 r.p.m. for 17 minutes and the 1½ gram sample of the liquid phase titrated in an alcohol-water solvent with sodium hydroxide. The millimoles of titrated acid, i.e., the amount of acid peptized by the oil, were reported. In this test, the base oil was a mid-Continent SAE 30 hydrocarbon oil and 2.0 weight percent of the polyisobutylenesuccinimide used in the aforementioned Falex Machine test. The test additive was added to this base oil in an amount sufficient to produce a concentration of 6 mM. phosphorus per kg. of total blended base oil and additive.

TABLE IV

Additive:	Acid titrated, mM.
Salt A	0.335
Composition of:	
Example 9	0.69
Example 17	0.71

It is evident from these data that the compositions of this invention substantially increase the effectiveness of detergents with which they are combined in lubricating oils, when compared to similar combinations of detergents with conventional zinc dithiophosphates.

The compositions of this invention also show good performance in engine tests. This is illustrated by the data of Table V, below, which presents the results of a modified L–4 engine test. The standard L–4 engine test is described in Federal Test Method Standard No. 791a, as Method No. 3402. The oils herein were run in a modification of that test, in which the brake horsepower of the engine was increased from 30 to 60, thus increasing the severity of the test. The viscosity of the oil was determined at 8-hour intervals, and the test continued until the viscosity increase at 100° F. becomes excessive. The base oil in each case was the neutral oil described in the oxidation test above (Table I), containing 5 weight percent of the succinimide described above, and 0.1 weight percent of terephthalic acid.

TABLE V

Additive	Length of test, hrs.	Viscosity increase at 100° F., percent	Bearing weight loss, mg.	Varnish		Total sludge [3]
				Piston [1]	Total [2]	
Salt A	40	167	847	9.8	44.1	49.9
Composition of Example 16	56	35	289	9.9	49.7	49.5

[1] Scale: 0-10; 10 indicates completely clean.
[2] Scale: 0-50; 50 indicates complete freedom from varnish.
[3] Scale: 0-50; 50 indicates complete freedom from deposits.

It is evident from the data in Table V that while the oil containing the additive of this invention was run almost half again as long as was the oil containing Salt A, thus substantially increasing the stress on the oil, the viscosity increase and bearing weight loss were both reduced several-fold. Further, during this extended run, the piston remained almost totally free of varnish and sludge.

The examples and descriptions above are intended to be illustrative only. It will be evident to those skilled in the art that there are many other embodiments of this invention which do not depart from the scope and spirit thereof.

What is claimed is:

1. An antiwear and antioxidant composition prepared by reacting at a temperature in the range of from 140° C. to 200° C., (1) a saturated aliphatic hydrocarbon amine of from 1 to 6 nitrogen atoms and 1 to 50 carbon atoms per molecule, in which the nitrogen atoms are present in primary or second amino groups, and (2) a dihydrocarbyl dithiophosphoric acid or a Group II–A or II–B metal salt of a dihydrocarbyl dithiophosphoric acid, wherein each hydrocarbyl radical is of from 18 to 50 carbon atoms; and wherein the ratio of said amine to said acid or salt is in the range of 0.1 to 1 mole of amine per equivalent of acid or salt.

2. The composition of claim **1**, wherein said amine is a polyamine of from 2 to 5 nitrogen atoms and 2 to 12 carbon atoms per molecule.

3. The composition of claim **2**, wherein said amine is a polyamine having alpha and omega primary amino groups.

4. The composition of claim **3**, wherein said polyamine is of 2 to 6 carbon atoms and 2 to 3 nitrogen atoms.

5. The composition of claim **1**, wherein each hydrocarbyl radical is an alkaryl radical in which an alkyl substituent, containing a linear portion having on the average at least 8 carbon atoms, is bonded to a benzene ring.

6. The composition of claim **1**, wherein said ratio of amine to acid or salt is in the range of 0.25 to 0.5 mole of amine per equivalent of acid or salt.

7. The composition of claim **1**, wherein the reaction is conducted at a temperature of from about 150° C. to about 185° C.

8. The composition of claim **1**, wherein the Group II–A or II–B metal in said salt is calcium, barium, or zinc.

9. The composition of claim **1**, wherein said Group II–B metal is zinc.

10. An antiwear and antioxidant composition prepared by reacting at a temperature in the range of from about 150° C. to about 185° C., (1) ethylene diamine, and (2) zinc O,O-di(alkaryl)dithiophosphate, wherein the alkyl substituent of each alkaryl radical contains an average total of from 12 to 14 carbon atoms and a linear chain of 8 carbon atoms; wherein the ratio of said ethylene diamine to said zinc O,O-di-(alkaryl)dithioposphate is about 0.5 mole of diamine per equivalent of dithiophosphate.

11. An antiwear and antioxidant composition prepared by reacting at a temperature in the range of from about 150° C. to about 185° C., (1) diethylene triamine, and (2) zinc O,O-di(alkaryl)dithiophosphate, wherein the alkyl substituent of each alkaryl radical contains an average total of from 12 to 14 carbon atoms and a linear chain of 8 carbon atoms; wherein the ratio of said diethylene triamine to said zinc O,O-di(alkaryl)dithiophosphate is about 0.5 mole of triamine per equivalent of dithiophosphate.

12. An antiwear and antioxidant composition prepared by reacting at a temperature in the range of from about 150° C. to about 185° C., (1) tetraethylene pentamine, and (2) zinc O,O-di(alkaryl)dithiophosphate, wherein the alkyl substituent of each alkaryl radical contains an average total of from 12 to 14 carbon atoms and a linear chain of 8 carbon atoms; wherein the ratio of said tetraethylene pentamine to said zinc O,O-di(alkaryl)dithiophosphate is about 0.5 mole of pentamine per equivalent of dithiophosphate.

13. A lubricant composition having antiwear and antioxidation properties which comprises a major portion of an oil of lubricating viscosity and a minor portion of the composition of claim **1**.

14. The lubricant composition of claim **13**, wherein said oil is a hydrocarbon oil.

15. A lubricant composition having antiwear and antioxidation properties comprising a major portion of a hydrocarbon lubricating oil and 0.1 to 3.0 weight percent of the composition of claim **1**.

16. A lubricant composition having antiwear and antioxidation properties comprising a major portion of a hydrocarbon oil and 0.1 to 3.0 weight percent of the composition of claim **5**.

17. The lubricant composition of claim **13**, wherein said amine is a polyamine of from 2 to 12 carbon atoms and 2 to 5 nitrogen atoms, having alpha and omega primary amino groups.

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DANIEL E. WYMAN, Primary Examiner

I. VAUGHN, Assistant Examiner

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