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3,351,647

NITROGEN, PHOSPHORUS AND METAL CONTAINING COMPOSITION

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No Drawing. Filed May 14, 1963, Ser. No. 280,452

7 Claims. (Cl. 260—429.9)

ABSTRACT OF THE DISCLOSURE

Phosphorus- and nitrogen-containing compositions are prepared by reacting a metal salt of a phosphinodithioic acid, especially a zinc salt of a diarylphosphinodithioic acid, with an amine, especially an aliphatic amine having from one to about 40 carbon atoms. The compositions are useful as additives for lubricating oils and automatic transmission fluids, in which they act as oxidation inhibitors and anti-wear agents. They afford synergistic oxidation inhibition properties when used with phenyl beta-naphthylamine.

This invention relates to novel compositions which are suitable for use as additives in lubricating compositions and more particularly it relates to a new class of compositions which are effective to inhibit oxidation in lubricating compositions and prevent wear of the metal surfaces being lubricated.

It is known that when oils, such as conventional lubricating oils, are subjected to extended periods of use, especially at high operating temperatures, they tend to decompose and form complex and objectionable oxidation and decomposition products including peroxides and organic acids. These substances possess corrosive and other deleterious properties and, unless neutralized or counteracted, will attack and damage engine metallic parts. These acids, furthermore, may go through a chemical process whereby the molecules combine or polymerize into large aggregates to form lacquer-like deposits on or between the moving parts of the engine, causing excessive wearing or even sticking of operating parts. Even larger quantities of polymerization products remain dispersed in the partially oxidized oil and are readily precipitated to form a sludge when the engine cools or when the fresh oil is added to the engine. These precipitated sludges become caked on the heated metal surfaces and reduce the effective life of the engine by preventing proper functioning of the parts thereof, such as by gumming up the piston rings which prevents proper piston action, or by blocking the oil passages of small diameter through which the lubricating oil normally flows to the bearings, whereby bearing failures are caused.

Eliminating or minimizing the above effects on oils and engines has constituted a lubricating problem since the advent of the internal combustion engine and many proposals for its solution appear in the prior art. These proposed solutions include use of the more stable synthetic ester oils and inclusion of addition agents, commonly called antioxidants, in conventional and synthetic oils to impart antioxidation properties thereto. Within recent years, however, more effective means have been required to solve the problem in many instances.

In the automotive industry, for example, reducing oil reservoir size, removing cooling coils, replacing metal gears with plastic gears, and warranting extended service periods, viz., requiring oil changes upon every 6,000 miles of driving in contrast to the former 1,000 mile standard, are factors which have increased the severity and complexity of the aforesaid problem. Automatic transmission

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fluids, for example, are subjected to higher temperatures, increased air contact, and longer service periods.

Likewise, in the lubrication of jet turbine bearings, the design of more powerful turbines has led to an increase in the lubricant reservoir temperature and to greater difficulty in maintaining lubricant stability under the more severe conditions. For example, a lubricant which will operate satisfactorily at a reservoir temperature of 250° F. may sludge badly, build up viscosity, develop high acidity, and corrode metals at a reservoir temperature at 400° F.

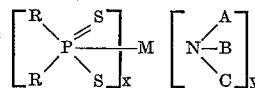
Among the objects of this invention, therefore, is that of providing new chemical compositions useful as antioxidants.

Another object of this invention is to provide methods of preparing these new chemical compounds.

Another object of this invention is to provide additives for lubricating compositions.

Still another object of this invention is to provide new lubricating compositions.

These and other objects are achieved by providing a phosphorus- and nitrogen-containing composition having the general formula



wherein R is a substantially hydrocarbon radical; M is a metal selected from the group consisting of zinc, calcium, copper, nickel, cobalt, chromium, lead, and cadmium; A, B, and C are radicals selected from the class consisting of hydrogen and substantially hydrocarbon radicals; x is the valence of M; y is from about 0.5 to about 6.

The R radicals of the nitrogen- and phosphorus-containing compositions of this invention may be the same or different radicals including alkyl, aryl, aralkyl, alkaryl, cycloalkyl, and heterocyclic radical, as well as such radicals containing substituents such as halogen, nitro, and the like. For reasons of economy and thermal stability, the aryl and alkaryl radicals are preferred, especially alkaryl radicals containing from 7 to about 26 carbon atoms.

A, B, and C of the nitrogen- and phosphorous-containing compositions may be hydrogen or a substantially hydrocarbon radical. Substantially hydrocarbon radicals represented by A, B, and C include alkyl, alkylol, aryl, aralkyl, alkaryl, cycloalkyl, aminoalkyl, and polyaminopolyalkene. These hydrocarbon radicals may contain from 1 to about 40 carbon atoms. However, where oil-solubility is a criterion, preferably, A and B are hydrogen radicals and C is an aliphatic radical containing at least about 12 carbon atoms.

The value of y may range from about 0.5 to about 6 and preferably is within the range of from about 1 to about the valence of the metal (M), i.e., x. The exact chemical structure of the composition is not known.

In the paragraphs to follow, reference is made to "equivalent" weights of reactants used in processes to provide the compositions of this invention. The term "equivalent" is based upon a consideration of the number of functional groups in a reactant, i.e., if there are two functional groups, then the equivalent weight is one-half the molecular weight. For the purposes of this specification, an equivalent weight of an amine will be that weight of amine containing one atomic weight of nitrogen and an equivalent weight of a phosphinodithioic acid or metal salt thereof will be that weight of phosphinodithioic acid or metal salt thereof containing one atomic weight of phosphorus.

The compositions of this invention may be prepared by reacting the metal salt of a phosphinodithioic acid

with an amine. The indicated reaction between the amine and the metal salt is often exothermic and may be carried out in many cases simply by mixing the reactants at room temperature. It is preferred to carry out the reaction at a temperature from about 10° C. to about 150° C.

The use of a solvent for the reaction mixture is contemplated and sometimes is especially advantageous.

The novel compositions of this invention may be prepared, alternatively, by first forming a complex of the inorganic metal component with ammonia or an amine, followed by a double decomposition reaction of this inorganic metal complex with the sodium or potassium salt of a phosphinodithioic acid. For example, a complex-forming metallic salt, such as zinc sulfate, may be reacted with ammonium hydroxide to form zinc ammonium sulfate; this is further reacted with the sodium salt of diphenyl phosphinodithioic acid to form a composition of this invention. Although the latter method is quite satisfactory in some instances, the former method is preferred.

The metal salt reactants employed as above for producing compositions of this invention are derivatives of phosphinodithioic acids conforming to the general formula



wherein R is a substantially hydrocarbon radical. The R groups of the phosphinodithioic acid may be the same or different radicals including alkyl, aryl, aralkyl, alkaryl, cycloalkyl, and heterocyclic radicals, as well as such radicals containing substituents such as halogen, nitro, and the like. For reasons of economy and thermal stability, aryl and alkaryl radicals are preferred.

The phosphinodithioic acids may be prepared by the reaction of Grignard reagents with phosphorus pentasulfide (see *Organo Phosphorus Compounds*, G. M. Kosolapoff, p. 135, John Wiley and Son, New York, 1950). The preferred and more economical method for preparing the phosphinodithioic acid is that described in U.S. 2,797,238 wherein aromatic compounds having ionization constants less than 1×10^{-10} in water at 25° C. and having at least one hydrogen atom attached to an aromatic ring structure are reacted with P_2S_5 in the presence of AlCl_3 in amounts such that the ratio of moles of AlCl_3 to moles of P_2S_5 is at least one. The preparation of alkyl aryl phosphinodithioic acids is accomplished by the reaction of an alkyl thiophosphine sulfide with an aromatic compound in the presence of aluminum chloride (see description by Newallis et al. in vol. 27, *Journal of Organic Chemistry*, page 3829).

Examples of aromatic radicals are organic radicals containing at least one resonant ring structure, such as phenyl, naphthyl, anthracyl, phenanthryl, naphthacyl, crslyl, pyryl, tribenzyl, biphenyl, and terphenyl radicals, and the substitution products of these such as their alkylation products, halogenation products, nitration products, etc. Examples of the alkylation products include tolyl, xylyl, di-ethylphenyl, iso-propylphenyl, n-propylphenyl, tert-butylphenyl, di-tert-butylphenyl, iso-butylphenyl, n-butylphenyl, tert-amylphenyl, cyclohexylphenyl, methyl-cyclohexylphenyl, caprylphenyl, diisobutylphenyl, dioctylphenyl, laurylphenyl, cetylphenyl, paraffin wax substituted phenyl, dodecylphenyl, di-dodecylphenyl, etc. Examples of halogenation products include chlorophenyl, 2,6-dichlorophenyl, trichlorophenyl, 4-bromophenyl, mono- and poly-chloroxenyl, mono- and poly-chloronaphthyl, mono- and poly-chloroanthracyl, methyl chlorophenyl, ethyl chlorophenyl, ethyl chloroanthracyl, etc. Examples of nitro products include nitrophenyl, nitroxenyl, methyl-nitrophenyl, butyl-nitrophenyl, etc.

The salts of the organic phosphinodithioic acids used in preparing the novel compositions of this invention can be prepared by the usual salt forming reactions. These

include the reaction of an organic phosphinodithioic acid with a metal powder, a metal hydroxide or metal oxide and the double decomposition reaction of the sodium or potassium salt of an organic phosphinodithioic acid with a metal halide or other suitable metal salt. The metals which may be used in accordance with the principle of this invention include zinc, calcium, copper, nickel, cobalt, chromium, lead, and cadmium. These metals may be incorporated in salts by direct reaction of a phosphinodithioic acid with, for example, zinc oxide, zinc hydroxide, calcium hydroxide, cuprous oxide, cupric oxide, nickel carbonate, cobaltous carbonate, or lead oxide, or by the double decomposition reaction of a sodium or potassium salt of a phosphinodithioic acid with, for example, cobaltous chloride, cobaltous nitrate, chromic nitrate, or chromous acetate.

Alternatively, in the case of certain zinc salts, the method described in U.S. 2,809,979 may be employed, wherein a mixture of aromatic compounds selected from the class consisting of aromatic hydrocarbons and halogenated aromatic hydrocarbons, phosphorus pentasulfide, an aluminum halide selected from the class consisting of aluminum chloride and aluminum bromide, and a zinc halide selected from the class consisting of zinc chloride and zinc bromide, is heated at a temperature within the range of about 130° C. to about 250° C.

Ammonia and many amines may be used to form the nitrogen and phosphorus-containing compositions of this invention. Broadly, the N-containing reactants useful in producing the compositions of this invention conform for the most part to the structural formula



wherein A, B, and C are radicals selected from the class consisting of hydrogen, alkyl, alkylol, aryl, aralkyl, alkaryl, cycloalkyl, aminoalkyl, and polyaminopolyalkylene. It will be appreciated that two of A, B, and C may be a single polyalkylene radical containing up to 5 carbon atoms. Preferably, at least one of A, B, and C is a hydrogen radical. This includes, for example, aliphatic amines, aromatic amines, polyamines, cyclo-aliphatic amines, heterocyclic amines, and carbocyclic amines. Specific examples of useful N-containing reactants include ammonia, ethylamine, propylamine, isopropylamine, butylamine, cyclohexylamine, n-hexylamine, dodecylamine, didodecylamine, tridodecylamine, N-methyl octylamine, N-dodecyltrimethylene diamine, ethanolamine, triethanolamine, guanidine, tripropylamine, aniline, o-toluidine, benzidine, phenylenediamine, N,N-di-sec-butylphenylene diamine, beta-naphthylamine, alpha-naphthylamine, morpholine, piperazine, methane diamine, cyclopentylamine, ethylene diamine, hexamethylene tetramine, octamethylene diamine, and N,N-dibutylphenylene diamine.

Aliphatic amines having from one to about 40 carbon atoms are preferred for the purposes of this invention. The preference is based largely upon the availability as well as the general compatibility with hydrocarbon materials, such as lubricating oils, paints, and fuels of the compositions of this invention derived from such amines. Examples of such aliphatic amines include tetracontylamine, tricontylamine, N-heptylhexylamine, methylethyl-i-propylamine, tirethylamine, octanol amine, and tripropanol amine. Especially useful in this sense are the tertiary alkyl primary amines containing from about 10 to about 80 carbon atoms.

Where oil-solubility of the novel compositions of this invention is required, primary aliphatic amines having more than about 12 carbon atoms are preferred, e.g., tert-dodecylamine, tert-octadecylamine, behenylamine, stearylamine, docosanylamine, hexacontanylamine, and pentaheptacontanylamine.

Examples of useful compositions of this invention include the complexes of one equivalent of tert-dodecyl-

amine with one equivalent of the zinc salt of di-xylylphosphinodithioic acid; one equivalent of tert-octadecylamine with one equivalent of the calcium salt of bis-(dichlorophenyl)phosphinodithioic acid; one equivalent of propylamine with one equivalent of the cadmium salt of di-(octylphenyl)phosphinodithioic acid; one equivalent of aniline with one equivalent of the cupric salt of di-(pentylphenyl)phosphinodithioic acid; two equivalents of ethylene diamine with the one equivalent of the cobaltic salt of di-(octylnaphthyl)phosphinodithioic acid; one equivalent of tert-dodecylamine with one equivalent of the zinc salt of chlorophenyl isopropylphenylphosphinodithioic acid; one equivalent of pentaheptacontylamine with one equivalent of the lead salt of di-(isopropylphenyl)phosphinodithioic acid; one equivalent of cyclohexylamine with one equivalent of the nickel salt of di-(ethylphenyl)phosphinodithioic acid; one equivalent of hexacontylamine with one equivalent of the cuprous salt of di-tolylphosphinodithioic acid; two equivalents of propylamine with one equivalent of the chromous salt of di-(octylphenyl)phosphinodithioic acid; three equivalents of ethylene diamine with one equivalent of the cobaltous salt of di-(octylnaphthyl)phosphinodithioic acid; one equivalent of docosanylamine with one equivalent of the zinc salt of diphenylphosphinodithioic acid; one equivalent of tert-octadecylamine with one equivalent of the zinc salt of di-(phenylthiophenyl)phosphinodithioic acid; one equivalent of stearylamine with one equivalent of the zinc salt of di-(chlorophenyl)phosphinodithioic acid; one equivalent of docosanylamine with one equivalent of the zinc salt of di-(pentylphenyl)phosphinodithioic acid; one equivalent of ethanolamine with one equivalent of the zinc salt of di-(pentylphenyl)phosphinodithioic acid; and one equivalent of tridodecylamine with one equivalent of the zinc salt of di-(pentylphenyl)phosphinodithioic acid.

The complexes or reaction products of this invention are, for the most part, quite readily soluble in hydrocarbon liquids such as toluene, xylene, heptane, and hexane. In fact, in many cases it is desirable to form the compounds of this invention in liquid hydrocarbon media.

Various specific embodiments of the invention as broadly defined above are included hereinafter for purposes of illustration only, and are not to be construed as limiting the invention in any way. All parts and percentages are by weight unless otherwise specified.

Example 1

A mixture of 1,485 grams (13.2 moles) of chlorobenzene and 666 grams (3 moles) of P_2S_5 is heated to 100° C. in 0.5 hour whereupon 998 grams (7.5 moles) of aluminum chloride is added. The resulting mixture is refluxed at 145° C. for 0.5 hour and then heated for 4 hours at 160–165° C. The product mixture is cooled and mixed with 1,914 grams of toluene. The toluene mixture is added slowly to 12 liters of vigorously agitated cold water, and then allowed to separate into layers. The water layer is discarded. The organic layer is mixed with a filtering aid and filtered. The filtrate, 2,835 grams, has an acid number of 81 (phenolphthalein) indicating that the toluene solution contains 4.1 equivalents of di-(chlorophenyl)phosphinodithioic acid.

This filtrate then is mixed with 82 grams of water and treated at 50° C. with 87 grams (2.1 equivalents) of zinc oxide over a period of 0.5 hour. To this reaction mixture at 80° C. there is added 88 grams (2.1 equivalents) more of zinc oxide throughout an additional period of 0.5 hour. The zinc oxide-treated material is heated at 80° C. for 1 hour, cooled to 49° C., mixed with 783 grams (4.1 equivalents) of a commercial aliphatic primary amine (which has an average molecular weight of 191 in which the aliphatic radical is a mixture of tertiary alkyl radicals containing from 11 to 14 carbon atoms), and heated for 1.5 hours at 90° C. The amine-treated material is mixed with 2,634 grams of mineral

oil, heated to 135° C./10 mm. to remove toluene, mixed with a filtering aid, and filtered. Analyses of the filtrate, a brown liquid, indicate a phosphorus content of 2.7%, a sulfur content of 6.0%, a zinc content of 2.8%, a nitrogen content of 1.2%, and a chlorine content of 5.98%.

Example 2

A mixture of 667 grams (1 equivalent) of a 50% toluene solution of di-(chlorophenyl)phosphinodithioic acid and 30 grams of water is heated to 40° C. To the reaction mixture at 40° C. there is added 65 grams (1.1 equivalents) of nickel carbonate whereupon the temperature rises to 50° C. The nickel carbonate treated material is heated at 90° C. for 1.5 hours, then subjected to azeotropic distillation to remove water. To the water-free mixture at 75° C. there is added 191 grams (1 equivalent) of the commercial aliphatic amine described in Example 1. The amine-treated material is heated at 90° C. for 1.5 hours, mixed with 377 grams of mineral oil, heated to 135° C./10 mm., mixed with a filtering aid, and filtered. Analyses of the filtrate, a red-brown liquid, indicate a phosphorus content of 2.6%, a sulfur content of 6.0%, a nickel content of 2.4%, and a chlorine content of 4.1%.

Example 3

To a mixture of 1,584 grams (13.2 moles) of cumene and 666 grams (3 moles) of P_2S_5 at 95° C. there is added 998 grams (7.5 moles) of aluminum chloride. The aluminum chloride treated material is heated at 115° C. for 6 hours, cooled to 30° C. and mixed with 2,400 grams of toluene. The toluene solution is added with stirring, to 12 liters of water over a period of 0.5 hour. The water layer is discarded; the organic layer is mixed with a filtering aid and filtered. The filtrate, 3,006 grams, has an acid number of 87 (phenolphthalein) indicating that the toluene solution contains 4.7 equivalents of di-(isopropylphenyl)phosphinodithioic acid. To the toluene solution at 50° C. there is added 197.5 grams (2.6 equivalents) of cuprous oxide. To the mixture at 80° C. there is added an additional 197.5 grams (2.6 equivalents) of cuprous oxide and a temperature rise to 85° C. of the reaction mixture is noted. The cuprous oxide treated material is held at 85° C. for 1 hour, cooled to 50° C., mixed with 898 grams (4.7 equivalents) of the commercial aliphatic amine described in Example 1, heated to 90° C. for 1.5 hours, mixed with 2,766 grams of mineral oil, heated to 150° C./10 mm., mixed with a filtering aid, and filtered. Analyses of the filtrate indicate a phosphorus content of 1.7%, a sulfur content of 3.3%, a copper content of 3.7%, and a nitrogen content of 1.2%.

Example 4

To a mixture of 167 grams (0.25 equivalent) of a 50% toluene solution of di-(chlorophenyl)phosphinodithioic acid and 167 grams of methanol at 25° C. there is added 10 grams (0.27 equivalent) of calcium hydroxide whereupon the temperature rises to 55° C. The reaction mixture is heated for one hour at 68° C., mixed with 48 grams (0.25 equivalent) of the aliphatic amine described in Example 1 at 60° C., held at 68° C. for 1.5 hours, mixed with 133 grams of mineral oil, heated to 135° C./10 mm., mixed with a filtering aid, and filtered. Analyses of the filtrate indicate a phosphorus content of 2.9%, and a calcium content of 1.3%.

Example 5

To a mixture of 1,214 grams (13.2 moles) of toluene and 666 grams (3 moles) of P_2S_5 at 100° C. there is added 998 grams (7.5 moles) of aluminum chloride. This mixture is heated at 135–140° C. for 4 hours, cooled to 25° C. and mixed with 1,668 grams of toluene. The toluene solution is added slowly to 12 liters of vigorously agitated cold water and the water layer is discarded. The organic layer is mixed with a filtering aid and filtered. The filtrate (2,756 grams) has an acid number of 92 (phenolphthalein) indicating that the toluene solution contains

4.5 equivalents of di-(methylphenyl)phosphinodithioic acid. To the toluene solution at 50° C. there is added over a period of 0.5 hour, 95.5 grams (2.35 equivalents) of zinc oxide, and then an additional 95.5 grams (2.35 equivalents) of zinc oxide is added at 80° C. The zinc oxide treated material is heated at 85° C. for 1.5 hours, cooled to 60° C., mixed with 860 grams (4.5 equivalents) of the commercial aliphatic amine described in Example 1, heated for 1.5 hours at 90° C., mixed with 2,596 grams of mineral oil, heated to 135° C./10 mm., mixed with a filtering aid, and filtered. Analyses of the filtrate, a reddish brown liquid, indicate a phosphorus content of 2.9%, a sulfur content of 6.3%, a zinc content of 2.9%, and a nitrogen content of 1.2%.

Example 6

To a mixture of 76 grams (0.4 equivalent) of the commercial aliphatic amine described in Example 1 and 198 grams of mineral oil at 400° C. there is added 122 grams (0.4 equivalent) of the zinc salt of dipenylphosphinodithioic acid. The mixture is heated for 3 hours at 90–100° C., mixed with a filtering aid, and filtered. Analyses of the filtrate, a yellow-brown liquid, indicate a phosphorus content of 2.5%, a sulfur content of 5.6%, a zinc content of 9.7%, and a nitrogen content of 1.6%.

Example 7

To a mixture of 2,880 grams (24 moles) of isopropyl benzene and 666 grams (3 moles) of P_2S_5 at 95° C. there is added 998 grams (7.5 moles) of aluminum chloride. The aluminum chloride treated mixture is heated at 115° C. for 7.5 hours (until H_2S evolution is complete), cooled at room temperature and added to 12 liters of vigorously stirred water. The temperature rises to 65° C. The water layer is discarded; the organic layer, 2,977 grams, has an acid number of 77 (phenolphthalein) indicating the presence of four equivalents of di-(isopropylphenyl)-phosphinodithioic acid. To the acidic material at 60° C. there is added 171 grams (4.2 equivalents) of zinc oxide. The zinc oxide treated material is heated at 80° C. for 1 hour, cooled to 60° C., mixed with 764 grams (4.0 equivalents) of the commercial aliphatic amine described in Example 1, heated at 90° C., held for 1.5 hours at 90° C., mixed with 2,227 grams of mineral oil, heated to 150° C./10 mm., mixed with a filtering aid, and filtered. Analyses of the filtrate, a yellow-brown liquid, indicates a phosphorus content of 3.1%, a sulfur content of 6.2%, a zinc content of 2.4%, and a nitrogen content of 1.0%.

Example 8

To 3,264 grams (4.8 equivalents) of a toluene solution of bis-(trimethylphenyl)phosphinodithioic acid there is added at 50–80° C., 204 grams (5.0 equivalents) of zinc oxide. This zinc oxide-treated material is heated for one hour at 80° C., then to 3,216 grams of this mixture at 80° C. there is added 879 grams (4.6 equivalents) of the commercial aliphatic amine described in Example 1. The amine treated material is heated at 90° C. for 1.5 hours, mixed with 2,561 grams of mineral oil, heated to 150° C./20 mm., mixed with a filtering aid, and filtered. Analyses of the filtrate, a red liquid, indicate a phosphorus content of 2.6%, a sulfur content of 5.1%, a zinc content of 3.0%, and a nitrogen content of 1.1%.

Example 9

To 84 grams (0.25 equivalent) of a commercial aliphatic primary amine (which has an average molecular weight of 330 and in which the aliphatic radical is a mixture of tertiary alkyl radicals containing from 18 to 22 carbon atoms) there is added 102 grams (0.25 equivalent) of the zinc salt (87% pure) of di-(chlorophenyl)phosphinodithioic acid, at a temperature of 40° C. The reaction mixture is heated for five hours at 95–100° C., then filtered. The filtrate, 146 grams, is mixed with 147 grams of mineral oil and refiltered. Analyses of the re-

filtered product, a yellow-brown liquid, indicate a phosphorus content of 2.2%, a sulfur content of 4.7%, a zinc content of 2.3%, a nitrogen content of 1.0%, and a chlorine content of 3.3%.

Example 10

To 1,952 grams (2.28 equivalents) of a 50% toluene solution of the zinc salt of di-(isopropylphenyl)phosphinodithioic acid at 55° C. there is added 298 grams (1.14 equivalent) of dodecylaniline. The reaction mixture is heated for 1.5 hours at 90° C., then at 110° C. to remove water, mixed with a filtering aid, filtered, and heated to 110° C./10 mm. Analyses of the residue, a red-brown liquid, indicate a phosphorus content of 5.8%, a sulfur content of 12.1%, a zinc content of 6.8%, and a nitrogen content of 1.4%.

Example 11

The process of Example 10 is repeated except that ethanolamine (139 grams, 2.28 equivalents) is used in lieu of the dodecylaniline.

Example 12

The process of Example 10 is repeated except that di-isopropanolamine (304 grams, 2.28 equivalents) is used in lieu of the dodecylaniline.

Example 13

A mixture of 400 grams (1 equivalent) of the zinc salt (87% pure) of di-(chlorophenyl)phosphinodithioic acid and 150 grams (0.5 equivalent) of a commercial, primary, saturated aliphatic amine having 16 to 17 carbon atoms in the aliphatic radical is ground into a fine powder and added to a mixture of 100 grams (0.52 equivalent) of the commercial aliphatic amine described in Example 1 and 650 grams of mineral oil. The reaction mixture is heated for 3 hours at 137° C. and filtered. Analyses of the filtrate indicate a phosphorus content of 2.6%, a sulfur content of 5.4%, a zinc content of 2.5%, a nitrogen content of 1.1%, and a chlorine content of 5.1%.

Example 14

To 1,244 grams (2 equivalents) of a 50% toluene solution of di-(iso-propylphenyl)phosphinodithioic acid at 60–90° C., there is added 86 grams (2.1 equivalents) of zinc oxide. The zinc oxide-treated material is heated for one hour at 80° C., then mixed with 96 grams (0.5 equivalent) of the commercial aliphatic amine described in Example 1, heated for one hour at 90° C., mixed with 827 grams of mineral oil, heated to 150° C./20 mm., and filtered. Analyses of the filtrate, a green-brown solid at room temperature, indicate a phosphorus content of 3.5%, a sulfur content of 6.9%, a zinc content of 3.8%, and a nitrogen content of 0.5%.

Example 15

A mixture of 1,954 grams (13.2 moles) of amylbenzene and 666 grams (3 moles) of P_2S_5 is heated to 95° C. whereupon 998 grams (7.5 moles) of aluminum chloride is added. The resulting mixture is heated at 135° C. for 5 hours. The mixture is cooled and mixed with 2,340 grams of toluene. The toluene mixture is slowly added to 12 liters of vigorously agitated cold water, and then allowed to separate in layers. The water layer is discarded and the organic layer is filtered. The filtrate, 3,265 grams, has an acid number of 67 (phenolphthalein) indicating that the toluene solution contains 3.9 equivalents of di-(amylphenyl)phosphinodithioic acid. To the filtrate (toluene solution) at 50–80° C., there is added 167 grams (4.1 equivalents) of zinc oxide. The zinc oxide treated material is heated at 80° C. for one hour, mixed with 2,017 grams of mineral oil, further diluted with 250 grams of toluene, mixed with 372 grams (1.95 equivalents) of the commercial aliphatic amine described in Example 1, heated at 90° C. for 1.5 hours, then heated to 150° C./20 mm., and filtered. Analyses of the filtrate, a red-brown

liquid, indicate a phosphorus content of 3.2%, a sulfur content of 5.6%, a zinc content of 2.3%, and a nitrogen content of 0.7%.

Example 16

To 933 grams (1.5 equivalents) of a 50% toluene solution of di - (isopropylphenyl)phosphinodithioic acid at 30° C. there is added 61.5 grams (0.55 equivalent) of lead oxide. To the reaction mixture at 50° C. there is added 122.5 grams (1.1 equivalents) more of lead oxide. The reaction mixture is heated at 50° C. for 2 hours. To the reaction mixture at 50° C. there is added 495 grams (1.5 equivalents) of the commercial aliphatic primary amine described in Example 9. The amine-treated reaction mixture is heated at 85° C. for 2 hours, heated to 125° C./10 mm., mixed with 384 grams of mineral diluent oil, mixed with a filtering aid, and filtered. Analyses of the filtered product, a red-brown liquid, indicate a phosphorus content of 2.9%, a sulfur content of 5.4%, a lead content of 6.6%, and a nitrogen content of 1.5%.

Example 17

To 622 grams (1 equivalent) of a 50% toluene solution of di - (isopropylphenyl)phosphinodithioic acid at 30° C. there is added 15 grams (0.27 equivalent) of cobaltic oxide. To the reaction mixture at 50° C. there is added 29 grams (0.53 equivalent) more of cobaltic oxide. The reaction mixture is heated at 85° C. for 2 hours. To the reaction mixture at 70° C. there is added 330 grams (1 equivalent) of the commercial aliphatic primary amine described in Example 9. The amine-treated reaction mixture is heated at 80° C. for 1.5 hours, heated to 125° C./15 mm., mixed with 224 grams of mineral diluent oil, mixed with a filtering aid, and filtered. Analyses of the filtrate, a black liquid, indicate a phosphorus content of 3%, a sulfur content of 6.2%, a cobalt content of 2%, and a nitrogen content of 1.5%.

Example 18

To 622 grams (1 equivalent) of a 50% toluene solution of di - (isopropylphenyl)phosphinodithioic acid at 30° C. there is added 23 grams (0.36 equivalent) of cadmium oxide. To the reaction mixture at 50° C. there is added 47 grams (0.74 equivalent) more of cadmium oxide. The reaction mixture is heated at 85° C. for 2 hours. To the reaction mixture at 70° C. there is added 330 grams (1 equivalent) of the commercial aliphatic primary amine described in Example 9. The amine-treated reaction mixture is heated at 85° C. for 1.5 hours, heated to 115° C./10 mm., mixed with a filtering aid and filtered. Analyses of the filtered product, a yellow-brown liquid, indicate a phosphorus content of 4.1%, a sulfur content of 8%, a cadmium content of 8.8%, and a nitrogen content of 2.2%.

Example 19

To 1,050 grams (1.5 equivalents) of a 50% toluene solution of di - (isopropylphenyl)phosphinodithioic acid at 50° C. there is added 61 grams (1.65 equivalents) of calcium hydroxide. The temperature rises to 77° C. (exotherm). The reaction mixture is heated at 85-90° C. for 2 hours. To the reaction mixture there is added 180 grams (0.26 equivalent) more of a 50% solution of di - (isopropylphenyl)phosphinodithioic acid. The mixture is held at 85° C. for 1 hour. Water is removed from the reaction mixture by azeotropic distillation. Ammonia (26 grams or 1.5 equivalents) is added to the reaction mixture below the surface at a rate of 1 cubic foot per hour within 2 hours. The ammonia treated product is mixed with a filtering aid and filtered. Analyses of the filtered product, a red-brown liquid, indicate a phosphorus content of 5%, a sulfur content of 9%, a calcium content of 2.6%, and a nitrogen content of 1.8%.

Example 20

To 757 grams (1 equivalent) of a 50% toluene solution of di - (isopropylphenyl)phosphinodithioic acid at 50° C. there is added 87 grams (1.1 equivalents) of chromous oxalate monohydrate. The reaction mixture is heated at 90° C. for 2 hours. To the reaction mixture at 70° C. there is added 330 grams (1 equivalent) of the commercial aliphatic primary amine described in Example 9. The temperature rises to 80° C. (exotherm). The material is held at 90° C. for 1.5 hours and during this time the color of the material changes from violet to green. The product is heated at 125° C./10 mm. and then filtered twice. Analysis of the filtered product, a green liquid, indicates a phosphorus content of 2.4%, a sulfur content of 4.4%, a chromium content of 1.29%, and a nitrogen content of 1.0%.

As indicated above, the compositions of this invention are useful as additives for lubricating oils. The lubricating oils in which the additives of this invention are useful may be of synthetic, animal, vegetable, or mineral origin. Ordinarily, mineral lubricating oils are preferred by reason of their availability, general excellence, and low cost. For certain applications, oils belonging to one of the other three groups may be preferred. For instance, synthetic polyester oils such as didodecyl adipate and di - 2 - ethylhexyl sebacate are often preferred as jet engine lubricants. Normally the lubricating oils preferred will be fluid oils ranging in viscosity from about 40 Saybolt Universal seconds at 100° F. to about 200 Saybolt Universal seconds at 210° F.

The concentration of the phosphorus- and nitrogen-containing compositions of this invention to be used in a lubricant depends primarily upon the type of oil used and the nature of the service to which the lubrication composition is to be subjected. In most instances the concentration will range from about 0.001% to about 5% by weight of a lubricant.

The lubricating oil compositions of this invention may also contain other additives such as ashless dispersants, metal-containing dispersants, anti-foam agents, color-stabilizers, anti-freeze agents, pour point depressing agents, auxiliary oxidation-inhibiting agents, corrosion-inhibiting agents, metal-deactivating agents, de-emulsifying agents, extreme pressure improving agents, etc.

When the compositions of this invention are used in combination with phenyl beta-naphthylamine in a lubricating oil, an unusual oxidation inhibiting effect is noted.

Detergents useful in conjunction with the phosphorus- and nitrogen-containing compositions of this invention in lubricants include normal or basic salts of petroleum naphthenic acids, petroleum sulfonic acids, oil-soluble fatty acids, ashless detergents such as the reaction product of triethylene tetramine with an alkenyl substituted succinic anhydride having at least 50 carbon atoms in the alkenyl substituent, and a copolymer of 5 parts of beta-diethyl amino-ethyl acrylate with 95 parts of dodecyl methacrylate, etc. Others include barium mahogany sulfonate, the barium salt of the phosphorus acids obtained by the reaction of polyisobutene (molecular weight of 1000) with phosphorus pentasulfide, and the calcium salt of didodecyl benzene sulfonate.

Anti-foam agents include polymeric alkyl siloxanes, poly(alkyl methacrylates) and a condensation product of alkyl phenol with formaldehyde and an amine. Pour point depressing agents are illustrated by polymers of ethylene, propylene, or isobutene and poly(alkyl methacrylates). Corrosion- and oxidation-inhibiting agents include 4-methyl - 2,6 - di - tert - butylphenol, N,N' - sec - butyl phenylene diamine, basic metal petroleum sulfates, metal phenates, amines, benzylthiocyanates, etc. Film strength agents include, e.g., chlorinated paraffin oils containing from 20 to 70% of chlorine, chlorinated eicosane wax containing from 50 to 60% of chlorine, hexachloro-diphenyl ether, polychlorophenol, polychloro bis-phenol, etc. Oiliness agents include, e.g., methyloleate, oleic acid,

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stearic acids, sulfurized sperm oil, sperm oil, corn oil, etc. Viscosity index improvers include, e.g., polymerized and copolymerized alkyl methacrylates, polymerized butene, etc.

To prepare the final oil compositions, the compositions of this invention may simply be added to the oil at the appropriate concentration. Ordinarily, a concentrate of the additive is prepared by dissolving it in a limited amount of the oil, optionally with other additives, and the concentrate is then diluted with additional amounts of the oil to prepare the final oil composition. The following lubricants are set forth for the purpose of illustration. All percentages are by weight.

Example A

	Percent
SAE 20 mineral lubricating oil	98.0
Product of Example 7	2.0

Example B

Mineral lubricating oil having a viscosity of 99 SUS (Saybolt Universal seconds) at 100° F. to 39 SUS at 210° F. and viscosity index of 93	89.0
Neutral barium salt of the steam hydrolyzed reaction product of polyisobutene (molecular weight of 48,000) with phosphorus pentasulfide	7.0
Carbonated, basic barium salt of sperm oil acid	1.5
Product of Example 1	2.0
Polymeric alkyl acrylate VI improver and pour point depressant	0.48
Polymeric alkyl siloxane anti-foam agent	0.02

Example C

Synthetic polyester lubricating oil (trimethylolpropane ester of a C ₇ carboxylic acid) having a viscosity of 115 SUS at 100° F. to 42.4 SUS at 210° F. and a viscosity index of 145	96.5
Product of Example 1	3.5

Example D

Synthetic polyester lubricating oil described in Example C	97.5
Product of Example 1	1.5
Phenyl beta-naphthylamine	1.0

Example E

Synthetic polyester lubricating oil described in Example C	97.0
Phenyl beta-naphthylamine	2.98
Product of Example 1	0.02

Example F

Synthetic polyester lubricating oil described in Example C	93.5
Phenyl beta-naphthylamine	3.0
Product of Example 1	3.5

Example G

SAE 20 mineral lubricating oil	96.0
Phenyl beta-naphthylamine	0.01
Product of Example 7	3.49

Example H

SAE 20 mineral lubricating oil	99.97
Phenyl beta-naphthylamine	0.01
Product of Example 1	0.02

Example I

SAE 20 mineral lubricating oil	99.0
4-methyl-2,6-di-tert-butylphenol	0.999
Product of Example 7	0.001

Example J

Mineral oil as described in Example B	95.0
Carbonated, basic barium salt of phosphorus trichlo-	

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ride and chlorinated polyisobutene (100,000 molecular weight)	2.5
Tetraethylene pentamine acylated with a substituted succinic anhydride having a polyisobutenyl radical (molecular weight of 850) as substituent	1.5
Product of Example 8	1.0

Example K

SAE 30 mineral lubricating oil	97.0
Zinc O,O'(di-methylamyl)phosphorodithioate	2.0
Product of Example 1	1.0
Tetraethylene pentamine acylated with a substituted succinic anhydride having a polyisobutenyl radical having (molecular weight of 850) as substituent	2.5

Example L

SAE 20 mineral lubricating oil	92
Tetraethylene pentamine acylated with a substituted succinic anhydride having a polyisobutenyl radical (molecular weight of 850) as substituent	3
Product of Example 2	5

The compositions of this invention are useful for improving the wear properties of lubricating oils, when incorporated therein in additive quantities. The wear properties of a lubricant are measured by the Four Ball Wear test. In this test, four ½" diameter SAE 52100 steel balls are arranged in a tetrahedral formation and the top ball is made to rotate against the three bottom balls, the points of contact being lubricated by the test lubricant. The top ball is rotated at 600 r.p.m., loaded against the three bottom balls with a 40 kilogram weight, for a period of 2 hours. During the test, the lubricating oil and steel balls are maintained at a temperature of 200° F. At the end of the test, the steel balls are examined for wear, evidenced by circular scars at the indicated points of contact. The diameter of these scars is measured and reported as an average. The lubricant of Example B allows an average scar diameter of 0.40 mm., whereas a lubricant identical with Example B except that it does not contain the product of Example 1, allows an average scar diameter of 0.79 mm. This comparison indicates that the compositions of this invention are good anti-wear agents for lubricating oils.

The lubricant composition of Example B is further useful as an automatic transmission fluid; this is illustrated by its performance in the Chevrolet Powerglide Oxidation Test, CRC Designation L-39. This test consists of operating a Chevrolet passenger car Powerglide Transmission for 300 hours under the following conditions: transmission sump temperature, 275° F.; governor pressure, 55-70 p.s.i.; main line pressure, 85-95 p.s.i.; transmission speed, 1750-1800 r.p.m. This test is regarded in the industry as an important means for evaluating lubricating compositions for use in automatic transmissions. The lubricant is evaluated in terms of (1) the weight loss of the cindered bronze thrust washer due to corrosion, (2) the amounts of varnish and sludge formed on the clutch plates (expressed in terms of a numerical rating between 10, representing no varnish or sludge, and 0, representing maximum varnish or sludge) and (3) the amount of the overall varnish and sludge formed in the transmission (expressed as a numerical rating between 50, representing no varnish or sludge, and 0, representing a maximum amount of sludge or varnish). The lubricant composition of Example B passes this test in all respects with a 0.12% weight loss of the cindered bronze thrust washer, a clutch plate varnish rating of 10, a clutch plate sludge rating of 9.7, an overall varnish rating of 50, and an overall sludge rating of 48.

The utility of the compositions of this invention in synthetic lubricating oils (as in Examples C and D) is illustrated by the performance of particular lubricants in a severe oxidation test, a modification of the procedure indicated in MIL-L-6808D. In this test, air is bubbled

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through a 250-ml. sample of the test oil at 425° F. containing 1" x 1" x 0.032" panels of copper, titanium, silver, aluminum, and steel for 40 hours at a rate of 3.4 cu. ft./hr. The neutralization number of the oil sample is determined before and after the test according to ASTM designation D974-58T using alpha-naphthalbenzein indicator. Oil sample losses (i.e., due to vaporization) are measured at 5-hour intervals and the tested oil is replenished with fresh test oil sample. The percent increase of the viscosity of the test oil sample is also determined at 5-hour intervals and the weight loss of the metal samples determined at the end of the test. The lubricants of Examples C and D when subjected to this test, show the following:

TABLE I.—OXIDATION TEST AT 425° F.

	(1)	Example No.		(2)
		C	D	
Acid Number (alpha-naphthalbenzein):				
Original		3.4	1.17	0.07
Final		13.56	1.54	4.08
Percent Viscosity Increase:				
15 hrs.	716.5	12.2	5.76	
20 hrs.		56.5	6.32	8.7
25 hrs.		104.4	6.17	18.6
34 hrs.		457.0	9.05	52.5
Wt. Loss of Metal Piece (mg.) Cu.	-22.3	-18.9	-3.5	-9.05

¹ Base line, the synthetic polyester oil described in Example C.

² 97.5% of the polyester oil described in Example C plus 2.5% of phenyl beta-naphthylamine.

The results of the oxidation test, tabulated in Table I, indicate that compositions of this invention are useful oxidation inhibitors for synthetic polyester oils. The results also indicate that the compositions of this invention act synergistically with phenyl beta-naphthylamine as oxidation inhibitors in synthetic polyester oils. The synergism is indicated for lubricant compositions wherein from about 0.001 to about 5% by weight of a composition of this invention and from about 0.001 to about 5% by weight of phenyl beta-naphthylamine are incorporated. Lubricant compositions containing from about 1% to about 5% by weight of a composition of this invention and from about 0.5% to about 3% of phenyl beta-naphthylamine are preferred, since maximum oxidation inhibition is obtained from the combination when these limits are employed.

Although, as previously indicated, the compositions of this invention have utility as additives in lubricating oils, they are also useful for other purposes. For example, small amounts of the composition of this invention may be incorporated in gasolines and fuel oils as stabilizers or into paint films as oxidation inhibitors. Compositions of this invention are also useful as insecticides.

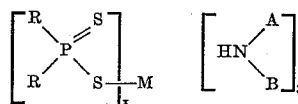
It is not intended that the examples and illustrations

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above limit the scope of this invention except as indicated in the appended claims.

What is claimed is:

1. An oil soluble nitrogen- and phosphorus-containing composition having the general formula



- wherein R is an aryl or halogen-substituted aryl radical, or an alkaryl radical containing from 7 to about 26 carbon atoms; each of A and B is hydrogen or an aliphatic hydrocarbon radical; M is zinc, calcium, copper, nickel, cobalt, chromium, lead or cadmium; x is the valence of M; and y is from about 0.5 to about 6.

2. The composition of claim 1 wherein M is zinc.

3. The composition of claim 1 wherein A is hydrogen and B is an aliphatic radical containing from 1 to about 40 carbon atoms.

4. The composition of claim 1 wherein A is hydrogen and B is an aliphatic radical containing at least about 12 carbon atoms.

5. The composition of claim 2 wherein



- contains from 1 to about 40 carbon atoms, at least one of A and B is an aliphatic hydrocarbon radical, and y is 1 or 2.

6. The composition of claim 5 wherein R is a chlorophenyl radical; y is 2; A is hydrogen and B is a tertiary alkyl radical containing from 8 to 30 carbon atoms.

7. The composition of claim 5 wherein R is an isopropylphenyl radical; y is 2; A is hydrogen and B is a tertiary alkyl radical containing from 8 to 30 carbon atoms.

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