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3,525,759

METAL ORGANO PHOSPHATES AND AMINE SALTS THEREOF

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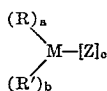
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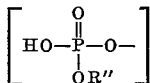
8 Claims

ABSTRACT OF THE DISCLOSURE

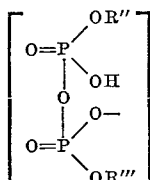
Metal organo phosphates and amine neutralization salts thereof having the formula:



wherein M is a polyvalent metal, R and R' are each selected from the group consisting of hydrogen and hydrocarbyl radicals of from 1 to 30 carbon atoms, a is an integer from 0 to 2, b is an integer from 1 to 3, c is an integer from 1 to 3, the sum of a plus b is an integer from 1 to 3, the sum of a plus b plus c is an integer from 2 to 4 and is equal to the valence of the metal, and Z is a radical selected from the group consisting of:



and



wherein R'' and R''' are each hydrocarbyl radicals of from 1 to 30 carbon atoms. These compositions are useful as gasoline and lubricating oil and additives.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a division of application Ser. No. 459,080 filed May 26, 1965, now Pat. No. 3,346,492, issued Oct. 10, 1967.

This invention relates to a novel class of organo phosphates and to amine adducts of such compounds. In other aspects, the invention relates to improved hydrocarbon compositions containing these novel compounds.

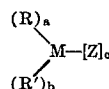
Normally liquid hydrocarbon products such as fuels and lubricating oils contain additives for improving the performance characteristics thereof. Thus, in fuels such as gasoline, additives are employed for improving various performance characteristics such as to assist in maintaining cleanliness of the carburetor, to resist surface ignition, and to inhibit rust and carburetor icing. Lubricating compositions contain various additives such as those for improving viscosity index and lubricity. The additives vary in effectiveness and it is often necessary to use a number of additives in a single composition.

The present invention provides a novel class of metal organo orthophosphates and a metal organo pyrophosphates which have been found to be beneficial for imparting carburetor and intake system detergency, rust

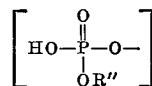
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suppression, inhibition of carburetor icing, reduction in octane requirement increase, and resistance to surface ignition of liquid hydrocarbon fuels, and friction and wear reduction in mineral oil lubricants. It has further been found that reaction produces of amines and such metal organo orthophosphates and pyrophosphates are especially advantageous for these purposes. It is to be understood that the term "metal" as used herein is intended to include silicon, which is normally considered to be a non-metal.

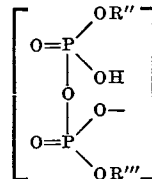
The class of metal organo phosphates provided by the present invention may be generically represented by the formula:



wherein M is a polyvalent metal, R and R' are each selected from the group consisting of hydrogen and hydrocarbyl radicals of from 1 to 30 carbon atoms, a is an integer from 0 to 2, b is an integer from 1 to 3, c is an integer from 1 to 3, the sum of a plus b is an integer from 1 to 3 and the sum of a plus b plus c is an integer from 2 to 4 and is equal to the valence of the metal and Z is a radical selected from the group consisting of:



and



wherein each of R'' and R''' are hydrocarbyl radicals of from 1 to 30 carbon atoms.

M in the above formula represents an element having a valence of 2 to 4 and selected from the group consisting of manganese, chromium, molybdenum, copper, gold and silicon, and the metals of Groups II, IV, and VIII of the Periodic Table. A suitable periodic table is shown on pages 392-393 of the Handbook of Chemistry and Physics 35th edition (1953). Tri and tetravalent metals are particularly preferred.

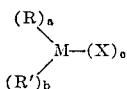
It can be seen from the formula that the metal organo orthophosphate and pyrophosphate compounds of the invention contain at least one acid (OH) group per molecule and have at least one hydrocarbyl or hydrogen radical bonded directly to the polyvalent element. Thus, R and R' may both be hydrogen or different or identical hydrocarbyl radicals of from 1 to about 30 carbon atoms, but preferably at least one R and R' represents a hydrocarbyl group radical. Typical hydrocarbyl radicals are, for example, alkyl, alkenyl, aryl, alkylaryl, arylalkyl, or alicyclic radicals. Exemplary of suitable hydrocarbyl radicals are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, isopentyl, hexyl, isohexyl, 2,2,4-trimethylpentyl, 2-methylpentyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, heptyl, 2-methylhexyl, 3-methylhexyl, 3,3-dimethylpentyl, octyl, 2,3-dimethylhexyl, 2,4-dimethylhexyl, 2-ethylhexyl, 2-ethylbutyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonyldecyl, eicosyl, hencosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triactonyl, phenyl, naphthyl, benzyl, o-cresyl, p-cresyl, n-cresyl, dodecylphenyl, octaphenyl, ethylphenyl, diphenyl, pentadecyl, β -

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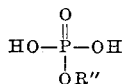
phenylethyl, omegaphenylhexyl, cyclohexyl, cyclobutyl, cyclopentyl, butenyl, octenyl, 2, - dimethylpentyl, 2-ethylhexenyl, linoleyl, oleyl, etc.

R'' and R''' in the above formula represents identical or different hydrocarbyl radicals having from 1 to 30 carbon atoms. Specific suitable hydrocarbyl radicals are those just-noted. Particularly preferred compounds for use as gasoline additives are those in which the hydrocarbyl radicals represented by R and/or R' are aliphatic hydrocarbyl radicals containing from 1 to about 18 carbon atoms and the hydrocarbyl radicals represented by R'' and R''' are aliphatic hydrocarbyl radicals containing from about 6 to about 22 carbon atoms, especially branched-chain aliphatic hydrocarbyl radicals of 6 to 22 carbon atoms.

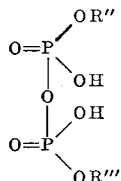
The compounds of the present invention may be prepared, for example, by reacting a compound of the formula:



wherein M, R, R', a, b, and c are as previously noted and X represents halogen, e.g. chlorine, with at least c moles of a monohydrocarbyl diacid orthophosphate having the formula:



wherein R'' is as previously noted, or with c moles of a dihydrocarbyl diacid pyrophosphate having the formula:

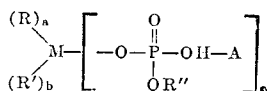


wherein R'' and R''' are as previously noted. Such monohydrocarbyl diacid orthophosphates and dihydrocarbyl diacid pyrophosphates may be prepared by reacting phosphorous pentoxide with an alcohol.

The reaction may conveniently be carried out at a temperature of between about 10° C. to about 120° C. in the presence of an inert solvent such as ether, a halogenated hydrocarbon, or an aliphatic or aromatic hydrocarbon. The reaction mixture thus obtained may or may not contain minor quantities of additional compounds, not all of which have been entirely identified, in addition to the compounds of the invention. Regardless of their identity, these extraneous compounds do not impair the effectiveness of the metal organo orthophosphates and pyrophosphates provided by the invention as gasoline and lubricant oil additives, and, therefore, need not be separated therefrom. Furthermore, although generally desirable, it is not necessary to separate the compounds of the invention from the solvent in which they are prepared prior to use.

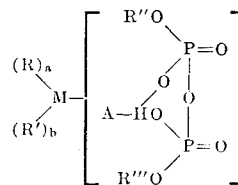
As mentioned hereinbefore, particularly useful gasoline and lubricant additives are obtained by reacting an amine with the metal organo orthophosphate and pyrophosphate compounds of the invention to form an amine adduct. Thus, the amine adducts are useful as lubricant additives, anti-corrosion additives, anti-icing additives, detergents, anti-stall additives, and reduce octane requirement increase in gasoline.

The amine adducts may be represented by the following formula:



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and



wherein R, R', R'', R''', M, a, b and c are as previously noted and A represents an amine containing from 1 to about 30 carbon atoms.

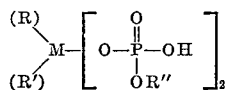
The amine adducts can be prepared by simply neutralizing the free acid (OH) group or groups of the metal organo orthophosphates and pyrophosphates. Formation of the adduct takes place at room temperature, although somewhat elevated temperatures such as that of about 100° F. are preferred. Preferably, each of the acid groups of the metal organo phosphate compounds is neutralized with basic nitrogen of the amine reactant, although this is not essential. Neutralization can be accomplished by simply adding the amine to the metal organo phosphate compounds to raise the pH thereof to at least 6 or 7. Also, the neutralization can be accomplished by adding a stoichiometric quantity of the amine to the metal organo phosphate compounds.

The amine employed in preparing the amine adducts of the present invention can be any salt-forming amine having from 1 to about 30 carbon atoms. Thus, primary, secondary, tertiary, aliphatic, aromatic or alicyclic amines may be used. The cyclic amines can be carbocyclic or heterocyclic. The amine can also be a mono-, di-, tri-, or other polyamine. Furthermore, the amine may be a β-amine and may contain various substituent groups such as hydroxyl groups. Preferred amines useful in the practice of the invention are aliphatic mono- or polyamines containing 6 to 22 carbon atoms arranged in an alkyl or alkenyl chain.

Illustrative of suitable amines for preparing the amine adducts of the metal organo orthophosphates and pyrophosphates there can be mentioned: methylamine, ethylamine, diethylamine, propylamine, tripropylamine, isopropylamine, butylamine, isobutylamine, hexylamine, 2-ethylhexylamine, octylamine, dodecylamine, 2-propyldecylamine, pentadecylamine, tetradecylamine, octadecylamine, 6-butyloctadecylamine, eicosamine, 6,6-dimethyl-1-propyldecylamine, 8-hexyl-10-isobutyloctadecylamine, dioctylamine, tribenzylamine, hexadecylamine, decylamine, N-hexyloctylamine, N,N-dimethyldodecylamine, oleylamine, linoleylamine, 1,10-decamethylenediamine, ethylenediamine, 1,2-propylenediamine, 1,12-dodecamethylenediamine, tetramethylenediamine, 1,6-hexamethylenediamine, triethylenetetramine, 1,2-phenylenediamine, benzylamine, 3,3'-biphenyldiamine, biphenylamine, 1-naphthylamine, 1-fluorenamine, aniline, N-methylaniline, N,N-dimethylaniline, 2,3-phenylenediamine, piperazine, piperidine, furfurylamine, N-cyclohexylheptylamine, and the like. The amines can also contain various substituent groups such as hydroxyl groups, e.g. alkanol amines, such as diethylanolamine, 3,3'-hydroxydipropylamine, isopropanolamine, and the like. β-amines, such as octyl-β-amine, can also be used. Mixtures of amines may also be used to prepare the amine adducts of the present invention. For instance, cocoamine, which is a mixture of amines prepared from coconut oil fatty acids and contains predominantly n-dodecylamine, and soya amine, which is a mixture of amines containing 16 to 18 carbon atoms, are especially suitable.

The novel organo orthophosphates and pyrophosphates and amine adducts thereof may be incorporated into gasoline composition in an amount between about 10 and about 500 parts per million parts of gasoline, by weight, preferably from 20 to about 250 p.p.m. and particularly from about 25 to 200 p.p.m. to improve the performance

characteristics thereof. The gasoline composition can be either leaded or unleaded, although leaded gasoline is preferred. In accordance with the preferred embodiment of the invention a gasoline composition is provided which comprises a major portion of leaded hydrocarbon vaporous fuel boiling in the gasoline range and containing between 10 and 500 p.p.m. of the amine adducts provided by the invention, and particularly the adducts obtained by reacting an aliphatic amine containing 6 to 22 carbon atoms with a metal organo orthophosphate represented by the formula:



wherein M is an element having a valence of 4, R and R' are each selected from the group consisting of hydrogen and aliphatic hydrocarbyl radicals of 1 to 18 carbon atoms, and R'' is an aliphatic hydrocarbyl radical of 6 to 22 carbon atoms. It will be understood that the terms "gasoline," "hydrocarbon base boiling in the gasoline range" and similar terms refer to a petroleum fraction boiling in a gasoline boiling range (e.g. between 50° F. and 450° F.). The term "leaded" gasoline refers to gasoline to which there has been added a small amount, such as between 0.1 and about 6.0 ml. per gallon of a metallo organic anti-knock compound such as a tetraethyl lead (TEL), tetramethyl lead (TML), tetraisopropyl lead, etc.

In addition to the additives of the present invention and optionally the lead anti-knock compounds, the gasoline compositions of this invention can also include, for instance, light hydrocarbon lubricating oils having viscosities at 100° F. of between about 50 and about 200 Saybolt Universal seconds (SSU) and viscosity indexes of between about 30 and about 130. Such oils may be present in suitable amounts such as between about 0.1 to about 1.0% by weight of gasoline composition.

When employed in lubricating compositions, such as lubricating oils, the novel compounds provided by the invention improve the boundary lubrication properties of the composition. Thus, lubricants containing the compounds of this invention inhibit the stick-slip sliding tendencies that are often found in automatic transmission clutching surfaces.

In preparing lubricant compositions with the additives of this invention, it has been found that the amount of additive can vary over a wide range, such as from 0.01% to about 10%, by weight, of the composition, and preferably from about 0.01% to about 3%, by weight, of the composition. The amine adducts are particularly desirable lubricating additives. In preparing lubricant compositions a wide variety of both mineral oil and synthetic base stock, including mixtures of the same, can be used. Suitable mineral oil base materials include 100 and 200 neutral oils, light and heavy intermediate mineral oils, bright stock as well as combinations of the foregoing. If a synthetic base material is used, it can be that of diesters, polyesters, silicones, silicates, fluorocarbons, phosphates and the like.

In addition to gasoline and lubricating oil compositions, the additives of the present invention may also be used in other hydrocarbon compositions. For example, they may be used in minor quantities of diesel fuel oil compositions to impart anti-rust activity, etc. to the composition.

Specific metal organo orthophosphate and pyrophosphate compounds and amine adducts are, for example:

monopropylcalcium mono[monoacid mono (propyl) orthophosphate]
monobutylberyllium mono[monoacid mono (hexyl) orthophosphate]
monoocetylberyllium mono[mono (octylammonium) di (octyl) pyrophosphate]
monoisobutylbarium mono[monoacid mono (isodecyl) orthophosphate]

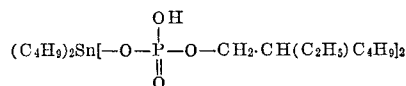
monoisobutylbarium mono[mono (cocoammonium) mono (isodecyl) orthophosphate]
monononylmagnesium mono[mono (oleylammonium) mono (octyl) orthophosphate]
5 monobenzylzinc mono[mono (isopropylammonium) di (benzyl) pyrophosphate]
mono-2-ethylhexylzinc mono[mono(2-ethylhexylammonium) mono (2-ethylhexyl) orthophosphate]
10 monoocetylcopper mono[monoacid mono (octyl) orthophosphate]
monoethylcopper mono[monoacid mono (butyl) mono (propyl) pyrophosphate]
monobenzylcadmium mono[monoacid mono (tricosyl) orthophosphate]
15 monoisodecylnickel mono[mono (isodecylammonium) mono (isodecyl) orthophosphate]
monophenyliron mono[monoacid mono (cyclohexyl) orthophosphate]
monopropylcobalt mono[monoacid mono (nonyl) orthophosphate]
20 monodecylmanganese mono[mono (isodecylammonium) mono (isodecyl) orthophosphate]
monohexylmanganese mono[monoacid di (ethyl) pyrophosphate]
25 amine adduct of aniline and monoheptylpalladium mono [monoacid mono (3-methylhexyl) orthophosphate]
monomethylchromium mono[monoacid mono (oleyl) orthophosphate]
30 monoethylplatinum mono[mono (heptadecylammonium) mono (2-ethylhexyl) orthophosphate]
monobenzylplatinum mono[mono (oleylammonium) di (lauryl) pyrophosphate]
monoheptylosmium mono[mono (pentylammonium) mono (pentyl) orthophosphate]
35 monobenzylgold di[monoacid mono (phenyl) orthophosphate]
diethylgold mono[mono (linoleylammonium) mono (ethyl) orthophosphate]
40 monoeicosyliron di[mono (laurylammonium) di (octyl) pyrophosphate]
dinaphthyliron mono[monoacid mono (2,2-dimethylbutyl) orthophosphate]
dinonyliron mono[mono (butylammonium) mono (nonyl) orthophosphate]
45 amine adduct of ethylene diamine and mono-p-cresyliron di [monoacid mono (p-cresyl) orthophosphate]
diisooctylnickel mono[monoacid mono (heptyl) orthophosphate]
monohexyliron di[mono (propylammonium) mono (octadecyl) orthophosphate]
50 amine adduct of triethylenediamine and monopropylnickel di [monoacid di (2,4-dimethylhexyl) pyrophosphate]
didodecylnickel mono[mono (cyclohexylammonium) mono (ethylphenyl) orthophosphate]
55 amine adduct of 1,6-tetrahexylenediamine and monocyclohexylnickel di [monoacid mono (tetracosyl) orthophosphate]
dibutylnickel mono[monoacid mono (butyl) orthophosphate]
60 monopropylcobalt di [mono (laurylammonium) di (propyl) pyrophosphate]
di (diphenyl) cobalt mono[monoacid mono (2,2-dimethylbutyl) orthophosphate]
monolinoleylcobalt di [mono (oleylammonium) mono (linoleyl) orthophosphate]
65 dipropylruthenium mono[monoacid mono (2-ethylhexyl) orthophosphate]
monoamylosmium di[mono (decylammonium) mono (decyl) orthophosphate]
70 monobenzylrhodium di[monoacid mono (cyclopentyl) orthophosphate]
diethylrhodium mono[monoacid di (isobutyl) pyrophosphate]
dimethylrhodium mono[mono (cocoammonium) mono (methyl) orthophosphate]

dipropyliridium mono[monoacid mono (undecyl) orthophosphate]
 di (2,4-dimethylhexyl) molybdenum mono[mono (cyclopentylammonium) mono (decyl) orthophosphate]
 monohexadecylmolybdenum di[monoacid mono (hexyldecyl) orthophosphate]
 diisooheptylchromium mono[monoacid mono (octyl) orthophosphate]
 diethylchromium mono[mono (octylammonium) mono (octyl) orthophosphate]
 dibutyltitanium mono[mono (methylammonium) mono (2-ethylhexyl) orthophosphate]
 monopentyltitanium di[mono (hexadecylammonium) mono (docosyl) orthophosphate]
 (monobutyl) (monopentyl) titanium mono[monoacid mono (octyl) orthophosphate]
 (monoocetyl) (monopentyl) titanium mono[mono (oleylammonium) di (hexacosyl) phosphate]
 mono- β -pentylethylmanganese tri[monoacid mono (octyl) orthophosphate]
 dipropylmanganese di [mono (tridecylammonium) di propyl) pyrophosphate]
 (monoethyl) (monopropyl) molybdenum di [monoacid di (ethyl) pyrophosphate]
 triocetylmolybdenum mono[mono (propylammonium) mono (butyl) orthophosphate]
 amine adduct of ethylenediamine and (monodecyl) (monododecyl) molybdenum di (monoacid mono (propyl) mono (butyl) pyrophosphate]
 (monopropyl) (monopentyl) titanium di [monoacid mono (hexyl) orthophosphate]
 dicyclohexyltitanium di [mono (cocoammonium) mono (benzyl) orthophosphate]
 triethyltitanium mono[monoacid mono (2-ethylhexyl) orthophosphate]
 monobenzyltitanium tri [mono (tripropylammonium) di (isopropyl) pyrophosphate]
 monoisodecyltitanium tri [mono (linoleylammonium) mono (isodecyl) orthophosphate]
 amine adduct of octyl- β -amine and dieicosyl titanium di [monoacid (heptyl) pyrophosphate]
 dimethyltitanium di [mono (oleylammonium) di (oleyl) pyrophosphate]
 tri (tert-butyl) hafnium mono[monoacid mono (tert-butyl) orthophosphate]
 tridocosylhafnium mono[mono (2-ethylhexylammonium) di (2-ethylhexyl) pyrophosphate]
 amine adduct of aniline and monomethylhafnium tri monoacid mono (octyl) orthophosphate
 dibenzylzirconium di [monoacid di (eicosyl) pyrophosphate]
 (monodecyl) (monododecyl) zirconium di [mono (propylammonium) mono (propyl) mono (butyl) pyrophosphate]
 tri-o-cresyl zirconium mono[mono (octylammonium) mono (octyl) orthophosphate]
 monobutylruthenium di [mono (cocoammonium) mono (butyl) orthophosphate]
 di-m-cresylruthenium di [monoacid do (m-cresyl) pyrophosphate]
 tridecylplatinum mono[monoacid mono (nonyl) orthophosphate]
 (monomethyl) (monoethyl) platinum di [mono (laurylammonium) di (butyl) pyrophosphate]
 monoleyloanium tri [mono (oleylammonium) di- β -phenylethyl pyrophosphate]
 monoocetylosmium tri [monoacid mono (octyl) orthophosphate]
 trihencosyliridium mono[mono (n-hexyloctylammonium) di (hencosyl) pyrophosphate]
 dicyclohexyltin di [monoacid mono (hexyl) orthophosphate]
 (monohydrogen) (monomethyl) tin di [mono (oleylammonium) mono (octyl) orthophosphate]

amine adduct of oleylpropylene diamine and diethyltin di-
 [monoacid mono (isopropyl) orthophosphate]
 mono-2-ethylhexyltin tri [mono (laurylammonium) di (octyl) pyrophosphate]
 triptylead mono[monoacid mono (heptyl) orthophosphate]
 triethyllead mono[mono (oleylammonium) mono (ethyl) orthophosphate]
 monohexylgermanium tri[mono (butylammonium) mono (lauryl) mono (oleyl) pyrophosphate]
 (monohydrogen) (monomethyl) silicon di [mono (oleylammonium) mono (octyl) orthophosphate]
 amine adduct of oleylpropylene diamine and dioctylsilicon di [monoacid mono (octyl) orthophosphate]
 15 This invention will now be further described with reference to the following specific and illustrative examples:

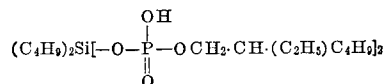
EXAMPLE 1

A solution of 100 g. (0.48 mole) of mono-2-ethylhexyl diacid orthophosphate in 50 ml. of heptane is added with stirring to 53 g. (0.17 mole) of dibutyltin dichloride diluted with 100 ml. of heptane. Air is bubbled slowly through the solution to aid the removal of HCl and the temperature is raised to 180° F. Heating is continued under reflux for 16 hours and the heptane is removed under vacuum. The product is dibutyltin di [monoacid mono (2-ethylhexyl) orthophosphate] as represented by the formula:



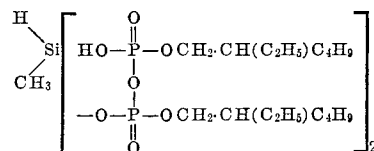
EXAMPLE 2

A solution of 100 g. (0.48 mole) of mono-2-ethylhexyl diacid orthophosphate in 100 ml. of heptane is added during 10 minutes with stirring to 45.5 g. (0.21 mole) of dibutylchlorosilane in 50 ml. of heptane. Air is bubbled through the solution to assist in the removal of HCl. The solution is then heated for 16 hours under reflux at 180° F. The solvent is removed under vacuum. The product remaining is dibutylsilicon di [monoacid mono (2-ethylhexyl) orthophosphate] having the formula:



EXAMPLE 3

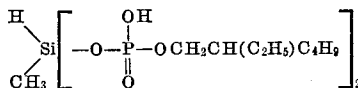
A solution of 100 g. (0.25 mole) of di-2-ethylhexyl diacid pyrophosphate in 100 ml. of heptane is added during 10 minutes with stirring to 14.25 g. (0.125 mole) of methylchlorosilane in 50 ml. of heptane. After 15 minutes, heat is applied and air is bubbled through the solution to remove HCl. Heating at 180° F. under reflux is continued for 16 hours and the solvent is removed under vacuum. The product remaining is (monohydrogen) (monomethyl) silicon di [monoacid di (2-ethylhexyl) pyrophosphate] having the formula:



EXAMPLE 4

A solution of 100 g. (0.48 mole) of mono-2-ethylhexyl diacid orthophosphate in 50 ml. of heptane is added during 10 minutes with stirring to a solution of 25 g. (0.22 mole) of methylchlorosilane in 50 ml. of heptane. Stirring is continued for 15 minutes before applying heat. Air is bubbled through the solution to remove HCl and the product is heated at 180° F. under reflux for 16 to

18 hours. The solvent is removed under vacuum. The residual product is (monohydrogen) (monomethyl) silicon di[monoacid mono (2-ethylhexyl) orthophosphate] having the structural formula:



The following example illustrates the preparation of representative amine adducts of this invention:

EXAMPLE 5

Portions of the product of Example 4 are mixed with oleylamine and oleylpropylene diamine, respectively, to obtain products having a pH of 7. The reactants are thoroughly mixed at room temperature while protected from carbon dioxide in a vessel blanketed with air.

The following example illustrates the preparation of lubricant compositions containing the oleylamine and oleylpropylene diamine adducts so prepared.

EXAMPLE 6

A measure of the boundary lubricating ability of each of the above-noted amine adducts in lubricating oil, and consequently their effectiveness in reducing wear, is obtained by means of a special apparatus used to assess the boundary properties of lubricants in a 50° F.-350° F. range. The measurement is reported as normal lubricity index, NLI, and values of 200 and above are considered very good. One part by weight of the various amine adducts is blended with 99 parts by weight of a neutral oil having a viscosity of 100 SUS at 100° F. The NLI values are given in the following tabulation.

Additive:	Normal lubricity index
None	100
Adduct of oleylamine and (monohydrogen) (monomethyl) silicon di [monoacid mono (2-ethylhexyl) orthophosphate]	237
Adduct of oleylpropylene diamine and (monohydrogen) (monoethyl) silicon di [monoacid mono (2-ethylhexyl) orthophosphate]	220

The following examples illustrate the use of the amine adducts of Example 5 as gasoline additives.

EXAMPLE 7

This example illustrates the use of the amine adduct additives in inhibiting icing in a spark ignition engine. A single cylinder engine is operated at constant speed with inlet air conditions controlled to promote carburetor icing. Test conditions are chosen to give an increase in manifold vacuum of 2.5 inches of mercury in 20 seconds with a base fuel. A clear plastic carburetor throttle body is used so that icing can be confirmed by visual inspection when desired. The base fuel is a mixture of equal parts by volume of isooctane and precipitation naphtha. Anti-icing is determined by noting the increase in time necessary to obtain a manifold vacuum of 2.5 inches of mercury by use of the base fuel (gasoline) containing the amine adduct as compared to the base fuel without such an amine adduct. The results of these tests wherein the time required for obtaining the specified vacuum is referred to as "stall time" are given in the following tabulation:

Additive	Concentration of additive (p.p.m.)	Percent improve- ment in stall time over base time
Oleylamine adduct	50	98.9
Do	30	61.3
Oleylpropylene diamine adduct	50	130.0
Do	30	118.6

EXAMPLE 8

Gasoline compositions are prepared by employing each of the amine adducts of Example 5 in an amount of 50 p.p.m. in a base gasoline having the following characteristics.

Distillation:

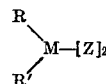
IBP—101° F.
10% evaporation—130° F.
20%—149° F.
30%—168° F.
50%—210° F.
70%—260° F.
90%—328° F.
End point—409° F.
Recovery—98.5%
Residue—1%
Gravity—58.2° API

ASTM rust tests are run at 70° F with each of the additive-containing gasoline compositions using distilled water. Each of the compositions passed the test.

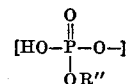
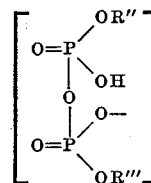
It will be understood that various changes in details herein described and illustrated in order to explain the invention may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims.

Therefore, I claim:

1. A compound having the formula:



wherein M is a polyvalent metal selected from the group consisting of silicon and tin, R and R' are each selected from the group consisting of hydrogen and hydrocarbyl radicals of from 1 to 30 carbon atoms, and Z is a radical selected from the group consisting of:

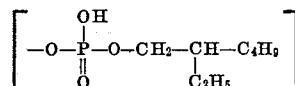


wherein R'' and R''' are each hydrocarbyl radicals of from 1 to 30 carbon atoms.

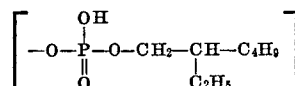
2. An amine adduct of the compound of claim 1 wherein said amine is an aliphatic amine containing from 1 to 30 carbon atoms.

3. An amine adduct of the compound of claim 1 wherein said amine is an aliphatic amine containing from 6 to 22 carbon atoms.

4. The compound of claim 1 wherein R and R' are both butyl radicals, M is tin and Z is

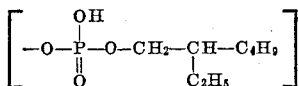


5. The compound of claim 1 wherein R and R' are both butyl radicals, M is silicon and Z is



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6. The compound of claim 1 wherein R is hydrogen, R' is a methyl radical, M is silicon and Z is



7. The oleylamine adduct of the compound of claim 6.

8. The oleyl propylenediamine adduct of the compound of claim 6.

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260—242, 268, 270, 293, 429, 429.3, 429.5, 429.9, 430, 431, 435, 438.1, 438.5, 439, 926, 930, 963, 964, 965, 448.2