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HYDROCARBON FUEL COMPOSITION

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This application is a continuation-in-part of my copending application Ser. No. 350,113, filed Mar. 6, 1964, for Process.

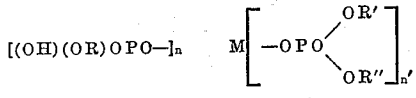
This invention relates to novel metal organo orthophosphates, novel amine salts of such orthophosphates and to hydrocarbon compositions containing the amine salts. The novel metal organo orthophosphates are certain metal (acid hydrocarbyl orthophosphates).

Normally liquid hydrocarbon products such as fuels and lubricating oils contain additives for improving their performance characteristics. Thus, gasolene 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.

It has now been found that certain metal (acid hydrocarbyl orthophosphates) and their amine salts are beneficial in imparting carburetor and intake system detergency, inhibition of rust, and inhibition of carburetor icing, reduction in octane requirement increase, and resistance to surface ignition of gasolene. Also, these compounds are good anti-wear agents for use in lubricants and fuels.

The novel amine salts of this invention are amine neutralization products of acid hydrocarbyl orthophosphates of a metal selected from the group consisting of manganese and the metals of Groups I–B, II, IV–A, VI and VIII of the Periodic Table. A suitable Periodic Table is shown on page 336 of the Handbook of Chemistry and Physics, 31st edition (1949). The metal (acid hydrocarbyl orthophosphate) intermediates of this invention can be represented by the formula:

FORMULA I



wherein M is a metal selected from the group consisting of manganese and the metals of Groups I–B, II, IV–A, VI and VIII; n is an integer from 1 to 4; n' is an integer from 0 to 3; the total of n and n' is equal to the valence of the metal M; and each of R, R′ and R″ is a hydrocarbyl group such as one having from 1 to about 30 carbon atoms.

The metal as represented by M in the above generic Formula I can be any metal selected from the group consisting of manganese and the metals of Groups I–B, II, IV–A, VI and VIII. The novel metal (acid hydrocarbyl orthophosphates) of Formula I and their corresponding amine salts are sometimes referred to herein collectively as additives. The amine salts are also referred to herein as ammonium derivatives or amine adducts additives, can have 1, 2, 3 or 4 acid groups (OH) per metal atom. Also, the total number of carbons can vary from about 4 to over 100, and preferably from about 4 to about 60 carbon atoms.

In the formulas used to describe compounds of this invention, such as Formula I above, R, R′ and R″ may represent identical or different hydrocarbyl groups. While any hydrocarbyl groups having between 1 and about 30 carbon atoms and soluble to the required extent in gasolene may be used, at least one of R, R′ and R″ preferably represents a branched chain hydrocarbyl group. Branched chain alkyl groups are especially suitable. Such groups are generally more soluble in gasolene than other hydrocarbyl groups, thereby facilitating the use of the novel compounds of the present invention as gasolene additives. Since chains of more than about 30 carbon atoms are generally difficult or impossible to dissolve in gasolene compositions, it is preferred that the hydrocarbyl groups of the additives of the present invention each have between 1 and about 30 carbon atoms. Typical R, R′ and R″ groups may include, for instance, alkyl, aryl, alkylaryl, arylalkyl, or alicyclic hydrocarbyl radicals. Examples of suitable hydrocarbyl radicals are: 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, triacontyl, phenyl, -naphthyl, benzyl, o-cresyl, p-cresyl, m-cresyl, dodecylphenyl, octylphenyl, ethylphenyl and diphenyl, pentadecyl, b-phenylethyl, omega phenylhexyl, cyclohexyl, cyclobutyl, cyclodecyl, cyclopentyl, etc. Corresponding unsaturated radicals may also be used.

The intermediate compounds of Formula I, i.e. the metal (acid hydrocarbyl orthophosphates) prior to neutralization of an acid group with an amine can be prepared by reacting a hydrocarbyl diacid orthophosphate which can be represented by the formula: $PO(OR)(OH)_2$ wherein R represents a hydrocarbyl group as in Formula I, or a mixture of a hydrocarbyl diacid orthophosphate and a di(hydrocarbyl) mono acid orthophosphate with a halide of the desired metal dispersed or dissolved in an inert organic solvent. The di(hydrocarbyl) mono acid orthophosphate can be represented by the formula:

$$PO(OR)_2(OH)$$

The intermediates of this invention can also be prepared by reacting a hydroxy compound, e.g. alkanol, alkenol or phenol with a metal halide of the desired metal and phosphorus pentoxide. This process permits direct synthesis of the intermediates from raw starting materials as described in my abovementioned copending application S.N. 350,113. In either method of preparation, identity of the hydrocarbyl groups present in the compounds represented by Formula I is determined by the identity of the hydrocarbyl groups present in the hydrocarbyl and phosphates or hydroxy compounds used as reactants.

The reaction temperatures are preferably from about 10° C. to about 120° C. and particularly from about 75° C. to about 90° C. About 2 to about 5 moles of the orthophosphate are usually reacted with each mole of the halide depending on the valence of the metal. However, the molar ratio of the reactants can vary over a wide range, e.g., in reacting the tetrahalides with a diacid mono (hydrocarbyl) orthophosphate or a mixture of the diacid and monoacid reactants about 3 to about 5 moles of the orthophosphate can be employed per mole of the tetrahalide. The inert solvent is preferably a hydrocarbon such as an aliphatic or aromatic hydrocarbon, e.g., benzene, toluene, heptane, octane, hexane, etc. However, the inert organic solvent need not be hydrocarbon, but instead any inert organic solvent such as an ether or halogenated hydrocarbon, e.g., ethyl ether, tetrahydrofuran, carbon tetrachloride, chlorobenzene, etc. can be employed.

In the above reaction wherein the phosphate reactant is a mixture containing both one and two acid groups per molecule, it is preferred that at least 10% by weight and

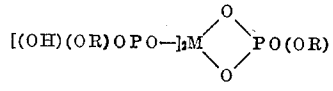
preferably at least 40% by weight of the mixture of orthophosphates be that of diacid mono (hydrocarbyl) orthophosphate since the monoacid dihydrocarbyl orthophosphates when reacted with the metal halides give compounds without a free acid group and therefore cannot be neutralized with an amine. Illustratively, the reaction of a diacid mono(hydrocarbyl) orthophosphate with nickel dichloride to prepare a nickel di [monoacid mono (hydrocarbyl) orthophosphate] can be shown by the equation:

$$NiCl_2+2PO(OR)(OH)_2 \rightarrow Ni[OPO(OR)OH]_2+2HCl$$

wherein R is hydrocarbon having from 1 to about 30 carbon atoms.

Use of a mixture of a diacid mono (hydrocarbyl) orthophosphate and mono acid di(hydrocarbyl) orthophosphate reactants with the metal reactants produces a mixture of products wherein some of the phosphate groups do not have four free hydroxyl groups but instead have less than four acid groups including a portion of the reaction product having no acid groups, e.g., a titanium tetra [di(hydrocarbyl) orthophosphate].

In addition to the compounds as represented by Formula I herein and those without a free acid group as can be produced by using the dihydrocarbyl orthopshosphate reactant, the reaction mixture often contains minor quantities of additional compounds not all of which have been entirely identified, including compounds wherein both acid groups of one or more of the diacid monohydrocarbyl orthophosphates become bound directly to the metal such as those of the following formula wherein one of the phosphate groups is bound to a tetravalent metal through two oxygen groups:



wherein M is a metal as hereinbefore described and each R is hydrocarbyl having 1 to about 30 carbon atoms. However, the mixture of compounds produced in the reaction can be neutralized with an amine without separation of the individual metal compounds or complexes and can be employed as additives to hydrocarbon fuels, e.g., gasolene, or lubricants. Also, it is not necessary, although generally desirable, to separate the metal compounds produced in the reaction or their amine salts from the solvent prior to use.

The amine, employed in preparing the amine additives of this invention can be any salt forming organic amine such as one having from 1 to about 30 carbon atoms. The amine can be primary, secondary or tertiary, aliphatic, aromatic or alicyclic. The cyclic amines can be carbocyclic or heterocyclic. The amine can be a mono-, di-, tri-, or other polyamine. The aliphatic amines as well as the aromatic and alicyclic amines can be those of hydrocarbons or hydrocarbons carrying various substitutes such as hydroxyl groups.

The following formulae illustrate various preferred amines which can be employed in accordance with this invention:

(a) $R^2-N(R)-R$; and (b) $R^2-N(R)-(CH_2)_n-N(R)-R^1$

wherein R is hydrocarbon, each R^1 and R^2 is hydrogen or hydrocarbon, n is an integer from 2 to about 10 and the total number of carbon atoms in each amine is from 1 to about 30. Preferably, R is aliphatic hydrocarbyl and each R^1 and R^2 is hydrogen or aliphatic hydrocarbyl. The aliphatic hydrocarbyl is preferably alkyl or alkenyl and particularly one having from 6 to about 24 carbon atoms.

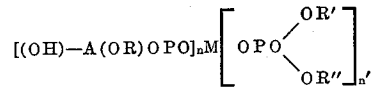
Illustrative of suitable amines for neutralizing the metal (acid hydrocarbyl orthophosphates) there can be mentioned: methylamine, ethylamine, diethylamine, propylamine, tripropylamine, isopropylamine, butylamine, isobutylamine, hexylamine, 2-ethylhexylamine, octylamine, dodecylamine, 2-propyldecylamine, pentadecylamine, tetradecylamine, octadecylamine, 6-butyloctadecylamine, eicosamine, 6,6-dimethyl-8-propyldecylamine, 8-hexyl-10-isobutyloctadecylamine, dioctylamine, tribenzylamine, hexadecylamine, decylamine, N-hexyloctylamine, N,N-dimethylodecylamine, oleylamine, linoleylamine, 1, 10-decamethylenediamine, ethylenediamine, 1,2-propylenediamine, 1,12-dodecamethylenediamine, tetramethylenediamine; 1,6-hexamethylenediamine, triethylenetetramine, 1,2 - phenylenediamine, benzylamine, 3,3′ - biphenyldiamine, 3 - biphenylamine, 1 - naphthylamine, 1 - fluorenamine, aniline, N-methylaniline, N,N-dimethylaniline, 1,3-phenylenediamine, 2-furanamine, piperazine, piperidine, furfurylamine, N-cyclohexylheptylamine, and the like. The amines can also contain various substituents on the hydrocarbon portion such as hydroxyl groups, e.g., alkanolamines, such as diethanolamine, 3,3′ hydroxydipropanolamine, isopropanolamine, and the like.

The hydrocarbyl radicals attached to the phosphates can be aliphatic, aromatic or cycloaliphatic, e.g., alkyl, alkenyl, aryl, aralkyl, alkaryl, etc. The aliphatic group can be saturated or unsaturated, e.g., containing mono-, di-, or polyolefinic unsaturation. The hydrocarbon groups as represented by R, R′ and R″ in Formula I can also contain various substituents such as halogen groups.

Illustrative of the diacid mono (hydrocarbyl) phosphates and monoacid di(hydrocarbyl) orthophosphate reactants there can be mentioned: diacid mono(octyl) orthophosphate, diacid mono(lauryl) orthophosphate, monoacid ethyl amyl orthophosphate, monoacid tertiary butyl isoamyl orthophosphate, di(2-ethylhexyl) monoacid orthophosphate, diacid mono(2-ethylhexyl) orthophosphate, diacid mono(n-octyl) orthophosphate, diacid mono (isooctyl) orthophosphate, monoacid isoamyl isooctyl orthophospate, diacid mono(nonyl) orthophosphate, monoacid di(nonyl) orthophosphate, monoacid methyl nonyl orthophosphate, diacid mono(cetyl) orthophosphate, diacid mono(tetradecyl) orthophosphate, diacid mono (stearyl) orthophosphate, monoacid di(eicosyl) orthophosphate, and diacid mono(eicosyl) orthophosphate. Illustrative of unsaturated aliphatic orthophosphates there can be mentioned: diacid mono(oleyl) orthophosphate, monoacid di(oleyl) orthophosphate, monoacid di(linoleyl) orthophosphate, monoacid oleyl lauryl orthophosphate, diacid mono(linoleyl) orthophosphate, monoacid ethyl linoleyl orthophosphate, diacid mono(4-heptenyl) orthophosphate, diacid mono(6-decenyl) orthophosphate, and the like. Illustrative of the phosphate reactant having an aryl group there can be mentioned those of phenyl, naphthyl and their substituted derivatives such as: monoacid di(benzyl) orthophosphate, diacid mono(benzyl) orthophosphate, monoacid ethyl benzyl orthophosphate, monoacid octyl phenyl orthophosphate, diacid mono (phenyl) orthophosphate, monoacid lauryl phenyl orthophosphate, monoacid di(naphthyl orthophosphate, diacid mono(naphthyl) orthophosphate, diacid mono(cresyl) orthophosphate, monoacid di(cresyl) orthophosphate, diacid mono(xylyl) orthophosphate, diacid mono(2-ethylphenyl) orthophosphate, and the like. Illustrative of phosphate reactants having a cycloaliphatic group there can be mentioned: monoacid di(cycloheptyl) orthophosphate, diacid mono(cycloheptyl) orthophosphate, monoacid di(ethylcycloheptyl) orthophosphate, diacid mono(cyclopentyl) orthophosphate, and the like.

The amine salts can be prepared by simply neutralizing the free acid group or groups of the metal (acid hydrocarbyl orthophosphates). Formation of the adduct can take place at room temperature although somewhat elevated temperatures such as that of about 100° F. is preferred. Preferably, each of the acid groups of the orthophosphate is neutralized with basic nitrogen of the amine reactant, although this is not necessary. Neutralization can be accomplished by simply adding the amine to raise the pH from less than about 5, of the unneutralized

compounds up to pH of at least 6 or 7. Also, the neutralization can be accomplished by adding a stoichiometric quantity of the amine to the particular metal (acid hydrocarbyl orthophosphate). Illustratively in the case of using a monoamine such as oleyl amine and neutralizing all the acid groups the amine adducts of this invention can be represented by the formula:



wherein M is a metal selected from the group consisting of manganese and the metals of Groups I–B, II, IV–A, VI and VIII; each of R, R′ and R″ is a hydrocarbyl having from 1 to about 30 carbon atoms; A is an amine; n is an integer from 1 to 4; n' is an integer from 0 to 3 and the total of n and n' is equal to the valence of the metal M.

The novel amine salts of this invention are useful as additives in liquid hydrocarbon compositions since they serve as lubricant additives, anti-corrosion additives, anti-icing additives, detergents, anti-stall additives, and reduce octane requirement increase of gasolene. For such use it is preferred that the hydrocarbyl portions of the orthophosphate have at least 6 carbon atoms, such as 6 to 22 carbon atoms and particularly wherein at least one hydrocarbyl group is branched, e.g., 2-ethylhexyl or 4-octylphenyl. Also, for such use it is preferred that the amine have at least 6 carbon atoms such as 6 to 24 carbon atoms, and particularly that the amine be that of an alkyl or alkenyl group which can be a mono- or diamine. The quantity of the novel amine salts in various compositions can vary over a wide range depending on the particular base stock to which they are added and their intended purpose. Thus, they can vary from about 10 parts per million by weight of the composition to over 10% by weight of the composition. The hydrocarbon compositions can be prepared by simply dissolving the amine salts in the hydrocarbon.

The novel metal (acid hydrocarbyl orthophosphates) and their amine salts are especially useful as gasolene additives to impart their above described properties. The gasolene composition can be either leaded or unleaded. Leaded gasolene is preferred. Thus in accordance with a preferred embodiment of the invention a gasolene composition is provided which comprises a major portion (at least about 50 volume percent) of leaded hydrocarbon base fuel boiling in the gasolene range and containing between about 10 to about 500 parts per million (p.p.m.) by weight, of the novel amine salts, preferably from about 20 to about 250 p.p.m. In addition to gasolene, the novel additives can be added to other hydrocarbon fuels in minor quantities such as in diesel oil to impart anti-rust activity, etc. to the composition. By the term "gasolene," "hydrocarbon base fuel boiling in the gasolene range" and similar terms is meant a petroleum fraction boiling in the gasolene boiling range (e.g., between about 50° F. and about 450° F.). The term "leaded" gasolene refers to gasolene to which there has been added a small amount, such as between 0.1 and about 6.0 ml. per gallon of a metalloorganic antiknock compound such as tetraethyl lead (TEL), tetramethyl lead (TML) tetraisopropyl, etc.

In addition to the novel amine salts and optionally the lead anti-knock compounds the gasolene compositions of this invention can include, for instance, light hydrocarbon lubricating oils having viscosities at 100° F. of between about 50 and about 200 Saybolt Universal seconds (SUS) and viscosity indexes of between about 30 and about 120. Such oils may be present in suitable amounts such as between about 0.1 and about 1.0 percent by weight of the gasolene composition.

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

In preparing lubricant compositions with additives of this invention it has been found that the amount of additive can vary over a wide range such as that of from 0.01% to about 10%, by weight, of the composition and preferably from about 0.1% to about 3%, by weight, of the composition. In preparing lubricant compositions a wide variety of both mineral oil and synthetic base stocks, 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.

Illustrative of novel additives of this invention, there can be mentioned the following amine salts and the corresponding metal (acid hydrocarbyl orthophosphates) from which these salts are derived by neutralization of acid groups:

nickel mono[di(2-ethylhexyl) orthophosphate] mono-[mono(cocoammonium) mono(2-ethylhexyl) orthophosphate],

germanium tetra[mono(laurylammonium) mono(2-ethylhexyl) orthophosphate],

manganese di[mono(laurylammonium) mono(2-ethylhexyl) orthophosphate],

beryllium di[mono(propylammonium) mono(4-octylphenyl) orthophosphate],

amine adduct of N-oleyl-1,3-propylene diamene and zinc bis[2-ethylhexyl, dibutynyl orthophosphate] bis[monoacid mono(2-ethylhexyl) orthophosphate],

amine adduct of hexamethylenediamine and chromium tri[monoacid mono(8-phenyloctyl) orthophosphate],

amine adduct of ethylenediamine and stannic bis[isobutyl, octylphenyl orthophosphate] bis[monoacid mono(isobutyl) orthophosphate],

iron III mono(laurylammonium) mono(2-ethylhexyl) orthophosphate] bis[2-ethylhexyl, octyl orthophosphate],

molybdenum bis[di(2-ethylhexyl) orthoprosphate] mono-[mono(oleylammonium) mono(2-ethylhexyl) orthophosphate],

magnesium mono[di(2-ethylhexyl) orthophosphate] mono[mono(laurylammonium) mono(2-ethylhexyl) orthophosphate],

cadmium mono[di(2-ethylhexyl) orthophosphate],

mono[mono(stearylammonium) mono(2-ethylhexyl) orthophosphate],

ruthenium di[mono(dioctylammonium) mono(4-octylphenyl) orthophosphate],[4-octylphenyl, methylethyl orthophosphate],

osmium di[mono(oleylammonium) mono(2-ethylhexyl) orthophosphate],

selenium tetra[mono(4-isopropylcyclohexylammonium) mono(2-ethylhexyl) orthophosphate],

nickel di[mono(oleylammonium) mono(oleyl) orthophosphate],

tungsten hexa[mono(benzylammonium) mono(eicosyl) orthophosphate],

lead tetra [mono(benzylammonium) mono(2,4-dimethyl-4-ethylheptyl) orthophosphate],

calcium di[mono(oleylammonium) mono(cycloheptyl) orthophosphate],

gold (III) tri[mono(laurylammonium) mono(2-ethylhexyl) orthophosphate],

cobalt (III) tri(monooleylammonium) mono(2-ethylhexyl) orthophosphate],

the amine adduct of triethylenediamine and rhodium di-[monoacid mono(cetyl) orthophosphate],

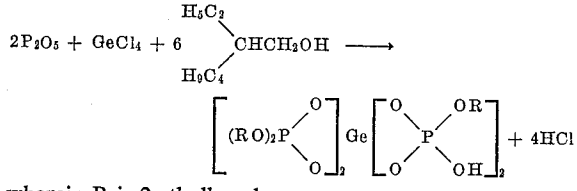
uranium (IV) tri[mono(decylammonium) mono(naphthyl) orthophosphate] mono[di(naphthyl) orthophosphate],

barium di[mono(oleylammonium) mono(benzyl) orthophosphate],
nickel (II) [mono(palmitylammonium) mono(linoleyl) orthophosphate] mono[di(linoleyl) orthophosphate],
piperazine adduct of copper di[monoacid mono(4-isopropylphenyl) orthophosphate],
the diethanolamine adduct of iridium di[monoacid mono-(3,4-dipropyleicosyl) orthophosphate],
the aniline adduct of radium di[monoacid mono(oleyl) orthophosphate],
the 1,4-phenylenediamine adduct of platinum mono-[monoacid mono(3-isopropylcyclohexyl) orthophosphate] mono[di(3-isopropylcyclohexyl) orthophosphate].

The following examples are illustrative of the preparation of the additives of the present invention:

Example 1

Germanium (IV) bis[di(2 - ethylhexyl) orthophosphate] bis[mono(2 - ethylhexyl) monoacid orthophosphate] is obtained from the reaction of 2 moles of phosphorus pentoxide and one mole of germanium tetrachloride with 6 moles of 2-ethyl-1-hexanol as shown below:



wherein R is 2-ethylhexyl.

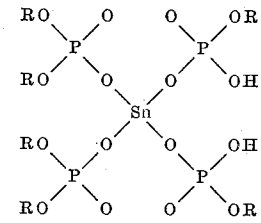
To a suitable reaction vessel equipped with a mechanical stirrer, stoppered pressure equalizing addition funnel, thermometer, gas inlet tube, and a reflux condenser protected with a drying tube, are added 400 ml. of anhydrous n-heptane and 71.0 g. (0.5 mole) or phosphorus pentoxide. With the stirrer going at a rate to insure a uniform dispersion 53.6 g. (0.25 mole) of germanium tetrachloride is added next. Finally 215 g. (1.65 moles) of 2-ethyl-1-hexanol, contained in the pressure equalizing addition funnel, is run into the reaction vessel at a rate such that the temperature of the reactants does not rise above 60° C. When this step is completed, the solution is homogeneous. The reactants are then heated at 98°–103° C., and when evolution of hydrogen chloride moderates, dry air is passed through the solution to displace the acid gas more rapidly and to accelerate the reaction. When further evolution of hydrogen chloride is no longer observed, as revealed by Congo Red indicator, the n-heptane and any unreacted octanol are removed by distillation in vacuo. The final temperature of the residual product in the reaction vessel is 175° at 25 mm. A product is obtained which is 99% of theory based on the metal halide.

Example 2

In the manner described in Example 1, 142 g. (1 mole) of P_2O_5 and 130 g. (1 mole) of anhydrous nickel chloride are dispersed uniformly in 1500 ml. of dry octane. Four hundred and thirty grams (3.3 moles) of 2,2,4-trimethyl-1-pentanol is added. The reaction mixture is heated at 105° C. until evolution of HCl stops. The solvent is removed by distillation in vacuo, the final temperature being 170° at 25 mm. pressure. The product is, nickel (II) [di(2,2,4 - trimethyl - 1 - pentyl) orthophosphate], [monoacid mono(2,2,4-trimethyl - 1 - pentyl) orthophosphate].

Example 3

Phosphorus pentoxide 71.0 g. (0.5 mole) and 65.1 g. (0.25 mole) of stannic chloride are dispersed in 500 ml. of toluene. A blend, consisting of 103 g. (0.5 mole) of octyl phenol and 74.1 g. (1 mole) of isobutanol, is added to the toluene dispersion in the manner described in Example 1. When evolution of hydrogen chloride is completed upon heating the reaction solution at 100° C. the solvent is removed by distillation at reduced pressure. The product can be represented by the following formula:



wherein four of the R groups are isobutyl

$$(CH_3CH(CH_3)CH_2—)$$

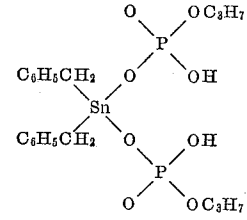
and the two remaining R groups are octylphenyl

$$[(CH_3)_3CCH_2C(CH_3)_2C_6H_5—]$$

in accordance with the stoichiometrical amounts required and used in the reaction.

Example 4

To a well stirred and dispersed mixture of 14.2 g. (0.1 mole) of P_2O_5 and 37.2 g. (0.1 mole) of dibenzyltin dichloride in 200 ml. of anhydrous n-heptane, there is added 18 g. (0.3 mole) of anhydrous isopropanol. When no more HCl is liberated at 98° C. the solvent is removed by distillation at reduced pressure, the final temperature being 150° C. The product is dibenzyltin bis[monoacid mono(isopropyl) orthophosphate] of the formula:



Example 5

Following the procedure of Example 1, the corresponding phenyl, benzyl, and cyclohexyl metal organo orthophosphates can be prepared by simply substituting the stoichiometric equivalent quantity of phenol, benzyl alcohol and cyclohexanol respectively for the 2-ethylhexanol employed in Example 1.

Example 6

One hundred grams of the product of Example 1 may be neutralized to form a salt with 75.2 grams of Alamine 11, a commercial oleylamine, in 69 grams of toluene by simply admixing the ingredients at about 100° F. The salt is soluble in toluene. Also, 100 grams of the mixture of Example 1 may be neutralized with 46 grams of Diam 11, oleyl-1,3-propylenediamine, to form a salt in 54.7 grams of toluene. The amine salt is soluble in toluene.

Example 7

Mono(2-ethylhexyl) diacid orthophosphate 84.0 gm. is dissolved in 200 ml. of toluene and added to 19 gm. of $SnCl_4$ dissolved in 150 ml. of toluene. The mixture is heated under reflux with nitrogen bubbling therethrough for four hours. The product in the reaction mixture is stannic tetra[mono(2-ethylhexyl) monoacid orthophosphate]. A portion of the reaction mixture containing 8.8 gm. of the product can be neutralized with 2.5 gm. of oleylamine to produce stannic tetra[mono(oleylammonium) mono(2-ethylhexyl phosphate]. Following the above procedure the corresponding amine salts can be prepared by simply substituting the stoichiometric equivalent quantity of isopropylamine, aniline, n-methyl cyclohexylamine, isopropanolamine, 6-hydroxyhexylamine, or 12-hydroxydodecylamine.

The following examples are illustrative of gasolene compositions of the present invention: It should be understood that any of the other novel additive compounds contemplated by the invention, such as those described above, may be used in such gasolene compositions in place of or in addition to the additives specified below.

Example 8

A gasolene composition affording rust inhibition, a reduction in octane requirement increase, protection against carburetor deposit buildup, suppression of surface ignition, and inhibition of carburetor icing can be prepared by dissolving germanium tetra[mono(oleylammonium) wherein the amine adduct is employed in a concentration mono (2-ethylhexyl) orthophosphate] in base gasolene of one pound for each 3,000 gallons of the composition. The base gasolene used in blending this and other gasolene compositions of the invention may be a gasolene having the following characteristics:

Distillation:

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

Example 9

Another suitable composition is that of a suitable base gasolene containing 0.1 ml. per gallon of TML and 100 p.p.m. by weight of nickel di[mono(laurylammonium) mono(2-ethylhexyl) orthophosphate].

Example 10

Another suitable composition can be prepared by dissolving two pounds of stannic bis[2 - ethylhexyl, octylphenyl orthophosphate] bis[mono(oleylammonium) mono(2-ethylhexyl) orthophosphate] in 3,000 gallons of gasolene containing 3 ml. of TEL per gallon.

Example 11

A suitable lubricating oil composition can be prepared by dissolving one pound of tin di[di(2-ethylhexyl) orthophosphate] di[mono(oleylammonium) mono(2-ethylhexyl) orthophosphate] in 12 gallons 200 neutral oil.

Example 12

A suitable lubricating oil composition can be prepared by dissolving one pound of molybdenum tri[mono(laurylammonium) mono(2-ethylhexyl) orthophosphate] in 15 gallons of a mineral lubricating oil.

Example 13

Another suitable gasolene composition contains 5 ml. of TEL per gallon and 500 p.p.m. by weight of molybdenum bis[di(2 - ethylhexyl) orthophosphate] mono [mono(oleylammonium) mono(2-ethylhexyl) orthophosphate].

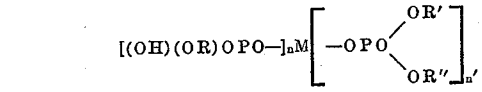
Example 14

Another suitable composition in base gasolene contains 1 ml. of TEL per gallon and 250 p.p.m. nickel mono[di (2 - ethylhexyl) orthophosphate] mono[mono(cocoammonium) mono(2-ethylhexyl) orthophosphate].

I claim:

1. A hydrocarbon fuel composition comprising a major portion of a liquid hydrocarbon fuel and a minor portion sufficient to provide anti-wear properties of a metal (acid hydrocarbyl orthophosphate) wherein the metal is selected from the group consisting of manganese and the metals of Groups I–B, II, IV–A, VI and VIII of the Periodic Table and wherein the acid of said orthophosphate is neutralized with an amine.

2. A gasolene composition comprising a major portion of leaded gasolene and between about 10 and about 500 p.p.m. by weight of an acid orthophosphate of the formula:



wherein each of R, R′ and R″ is a hydrocarbyl group of from 1 to about 30 carbon atoms, M is a metal selected from the group consisting of manganese and the metals of Groups I–B, II, IV–A, VI and VIII of the Periodic Table, *n* is an integer from 1 to 4, *n′* is an integer from 0 to 3 and the total of *n* and *n′* is equal to the valence of the metal M, and wherein said acid orthophosphate is neutralized with an amine.

3. A composition of claim **2** wherein at least one of R, R′ and R″ is a branched chain hydrocarbyl and the amine is aliphatic hydrocarbyl amine of from about 6 to about 24 carbon atoms.

4. A composition of claim **3** in which the metal is nickel.

5. A composition of claim **3** in which the metal is germanium.

6. A composition of claim **3** in which the metal is tin.

7. A composition of claim **3** wherein the amine is alkenylamine.

8. A composition of claim **3** wherein the amine is alkylamine.

9. A composition of claim **3** wherein the amine is diamine.

10. A composition of claim **3** in which the amine is cocoamine.

11. A composition of claim **3** wherein each of R, R′ and R″ is a branched chain alkyl hydrocarbyl group.

12. A composition of claim **11** in which the metal is nickel.

13. A composition of claim **11** in which the metal is germanium.

14. A composition of claim **11** in which the metal is tin.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,334,978 August 8, 1967

Anthony J. Revukas

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 1, 5 and 10, in the bracketed portions of the formulas, the OR' and OR'' groups should be indicated as being bonded to phosphorus rather than oxygen; column 3, line 56, for "substitutes" read -- substituents --; columns 7 and 8, in the formulas, the lines connecting oxygen molecules with phosphorus should be shown as arrows.

Signed and sealed this 15th day of October 1968.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents