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AMINE SALTS OF METAL ORGANO ORTHOPHOSPHATES

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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, 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.

It has now been found that amine salts of certain metal (acid hydrocarbyl orthophosphates) 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 liquid hydrocarbon fuels. Also, the amine adducts are good anti-wear agents for use in lubricants.

The novel amine salts of this invention are amine neutralization products of acid hydrocarbyl orthophosphates of a Group IV–B metal of the Periodic Table. A suitable Periodic Table is shown on page 336 of the Handbook of Chemistry and Physics, Thirty-first Edition (1949). The metal (acid hydrocarbyl orthophosphate) intermediates of this invention can be represented by the formula:

FORMULA I

$$[(OH)(OR)OPO—]_nM[—OPO(OR)_2]_{n'}$$

wherein M is a Group IV–B metal such as titanium, zirconium or hafnium; (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 R is a hydrocarbon 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 trivalent or tetravalent. It is preferred that M represent tetravalent titanium. It can be seen from Formula I that the metal (acid hydrocarbyl orthophosphates) and their corresponding amine salts which are also referred to herein as ammonium derivatives, amine adducts or simply 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. Preferably, the intermediate metal (acid hydrocarbyl orthophosphates) contain 2 or 4 acid groups, and can be represented by the following generic formulae respectively:

(a) $[(OH)(OR)OPO—]_2M[—OPO(OR)_2]_2$

and

(b) $M[—OPO(OR)(OH)]_4$

wherein R represents hydrocarbyl having from 1 to about 30 carbon atoms and M is tetravalent titanium or zirconium.

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 hydrocarbyl as in Formula I, or a mixture of a hydrocarbyl diacid orthophosphate and a di(hydrocarbyl) mono acid orthophosphate with a halide of a Group IV–B metal of the Periodic Table 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 Group IV–B metal halide and phosphorus pentoxide. This process permits direct synthesis of the intermediates from raw starting materials.

Illustrative of halides of Group IV–B metals there can be mentioned: titanium trichloride; titanium tetrachloride; zirconium tetrachloride; zirconium trichloride; titanium tetrabromide, hafnium tetrachloride; and the like. The reaction temperatures are preferably from about 40° C. to about 110° C. and particularly from about 75° C. to about 90° C. About 3 or about 4 moles of the orthophosphate are reacted with each mole of the halide depending on whether the metal is in the trivalent or tetravalent state respectively. 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 titanium tetrachloride to prepare a titanium tetra[monoacid mono(hydrocarbyl)orthophosphate] can be shown by the equation:

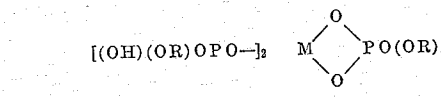
$$TiCl_4+4PO(OR)(OH)_2\rightarrow Ti[OPO(OR)OH]_4+4HCl$$

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 orthophosphate 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:

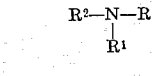


wherein M is a metal as hereinbefore described and each R is hydrocarbyl having 1 to about 30 carbon atoms. However, the mixture of compounds produced in the reaction can be neutralized with an amine without separation of the individual metal compounds or complexes and can be employed as adidtives to hydrocarbon fuels, e.g. gasoline, 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 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.

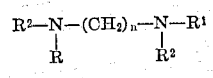
The following formulae illustrate various preferred amines which can be employed in this invention:

(a)



and

(b)



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-dimethyldodecylamine; oleylamine; lnioleylamine; 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-fluoroenamine; aniline; N-methylaniline; N,N-dimethylaniline; 2,3-phenylenediamine; 2-furanamine; piperazine; piperidine; furfurylamine; N-cyclohexylheptylamine; and the like. The amines can also contain various susbtituents on the hydrocarbon portion such as hydroxyl groups, e.g. alkanolamines, such as diethanolamine; 3,3'-hydroxydipropanolamine; isopropanolamine, and the like.

The hydrocarbyl radical attached to the phosphate 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 group as represented by 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 orthophosphate; 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; mono acid 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 - decanyl) 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 a 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:

$$[(OH)—A(OR)OPO]_nM[OPO(OR)_2]_{n'}$$

wherein M is a Group IV–B metal; 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, anticing additives, detergents, anti-stall additives, and reduce octane requirement increase of gasoline. For such use it is preferred that the hydrocarbyl portion of the orthophosphate have at least 6 carbon atoms, such as 6 to 22 carbon atoms and particularly wherein the hydrocarbon 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 amine salts are especially useful as gasoline additives to impart their above described properties. The gasoline composition can be either leaded or unleaded. Leaded gasoline is preferred. Thus in accordance with a preferred embodiment of the invention a gasoline composition is provided which comprises a major portion of leaded hydrocarbon base fuel boiling in the gasoline 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. and particularly from about 25 to 200 p.p.m. In addition to gasoline, the amine salts can be added to other hydrocarbon fuels in minor quantities such as in diesel oil to impart antirust activity, etc. to the composition. By the term "gasoline," "hydrocarbon base fuel boiling in the gasoline range" and similar terms is meant a petroleum fraction boiling in the gasoline boiling range (e.g. between about 50° F. and about 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 antiknock compound such as tetraethyl lead (TEL), tetramethyl lead (TML), tetraisopropyl, etc.

In addition to the novel amine salts and optionally the lead antiknock compounds the gasoline 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 gasoline composition.

When employed in lubricating compositions such as lubricating oils the novel amine salts improve the boundary lubrication properties of the composition. Thus, lubricants containing the novel amine salts 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 amine salts of this invention it has been found that an 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 amine salts of this invention, there can be mentioned: titanium bis [di(2-ethylhexyl) orthophosphate] bis [mono (cocoammonium) mono (2-ethylhexyl) orthophosphate]; hafnium tetra [mono (laurylammonium) mono (2-ethylhexyl) orthophosphate]; zirconium tetra [mono (laurylammonium) mono (2-ethylhexyl) orthophosphate]; zirconium tetra [mono (oleylammonium) mono (2-ethylhexyl) orthophosphate]; zirconium tetra [mono (propylammonium) mono (4-octylphenyl) orthophosphate]; amine adduct of N-oleyl-1,3-propylene diamine and zirconium bis [di(2-ethylhexyl) orthophosphate] bis [monoacid mono (2-ethylhexyl) orthophosphate]; amine adduct of hexamethylenediamine and titanium tetra [monoacid mono (8-phenyloctyl) ohtrophosphate]; amine adduct of ethylenediamine and titanium bis [di(isobutyl) orthophosphate] bis [monoacid mono (isobutyl) orthophosphate]; titanium (IV) mono (laurylammonium mono (2-ethylhexyl) orthophosphate] tri [di(2-ethylhexyl) orthophosphate]; titanium bis [di(2-ethylhexyl) orthophosphate] bis [mono (oleylammonium) mono (2-ethylhexyl) orthophosphate]; titanium bis [di(2-ethylhexyl) orthophosphate] bis [mono (laurylammonium) mono (2-ethylhexyl) orthophosphate]; titanium bis [di(2-ethylhexyl) orthophosphate] bis [mono (stearylammonium) mono (2-ethylhexyl) orthophosphate]; titanium tri [mono (dioctylammonium) mono (4-octylphenyl) orthophosphate] [di(4-octylphenyl) orthophosphate]; titanium tetra [mono(oleylammonium) mono(2-ethylhexyl) orthophosphate]; titanium tetra [mono(4-isopropylcyclohexylammonium) mono(2-ethylhexyl) orthophosphate]; titanium tetra[mono(oleylammonium) mono (oleyl) orthophosphate]; titanium tetra [mono(benzylammonium) mono (eicosyl) orthophosphate]; titanium tetra[mono(benzylammonium) mono (2,4-dimethyl-4-ethylheptyl) orthophosphate]; titanium tetra [mono(oleylammonium) mono (cycloheptyl) orthophosphate]; titanium (III) tri [mono (laurylammonium) mono (2-ethylhexyl) orthophosphate], zirconium (III) tri [mono(oleylammonium) mono (2-ethylhexyl) orthophosphate]; the amine adduct of triethylenediamine and titanium tetra[monoacid mono(cetyl) orthophosphate]; titanium (IV) tri[mono(decylammonium) mono (naphthyl) orthophosphate] mono [di(naphthyl) orthophosphate]; hafnium tri[mono(oleylammonium) mono (benzyl) orthophosphate]; titanium (IV) [mono(palmitylammonium) mono (linoleyl) orthophosphate] tri [di(linoleyl) orthophosphate]; piperazine adduct of hafnium [monoacid mono(4-isopropylphenyl) orthophosphate]$_4$; the diethanolamine adduct of titanium tri[monoacid mono(3,4-dipropyleicosyl) orthophosphate]; the aniline adduct of titanium tetra[monoacid mono(oleyl) orthophosphate]; the 1,4-phenylenediamine adduct of titanium bis[monoacid mono(3-isopropylcyclohexyl) orthophosphate] bis [di(3-isopropylcyclohexyl) orthophosphate].

The following examples are illustrative of the invention:

EXAMPLE 1

Two hundred grams of a mixture of orthophosphates containing 71.7% of mono (2-ethylhexyl) diacid orthophosphate and 28.3% of di (2-ethylhexyl) monoacid orthophosphate were added to 23.6 ml. of titanium tetrachloride in 250 ml. of heptane during fifteen minutes. The mixture was heated with stirring at about 200° F. while blowing with air to remove HCl. The mixture was held at about 200° F. for four hours and overnight with stirring and air bubbling very slowly through the mixture which appeared to be a solution. In the morning air bubbling was increased and continued for one half hour. The heptane solvent was removed under vacuum. The product was a mixture of various titanium compounds having 4 moles of phosphate per mole of titanium such as those of the following formulae wherein C_8H_{17} is 2-ethylhexyl:

(a) $Ti[OPO(OC_8H_{17})OH]_4$
(b) $Ti[OPO(C_8H_{17})_2]_4$
(c) $[(OH)(OC_8H_{17})OPO]_2Ti[OPO(C_8H_{17})_2]_2$
(d) $[(OH)(OC_8H_{17})OPO]Ti[OPO(C_8H_{17})_2]_3$
(e) $[(OH)(OC_8H_{17}OPO]_3Ti[OPO(C_8H_{17})_2]$

EXAMPLE 2

One hundred grams of the mixed product of Example 1 was neutralized to form a salt with 107.5 grams of Alamine 11, a commercial oleylamine, in 69 grams of toluene by simply admixing the ingredients at about 100° F. The salt was soluble in toluene. Also, 100 grams of the mixture of Example 1 were neutralized to form a

salt with Diam 11, oleyl-1,3-propylenediamine, in 54.7 grams of toluene. The amine salt was soluble in toluene.

EXAMPLE 3

By following the procedure of Example 1 but substituting the stoichiometric equivalent quantity of zirconium tetrachloride for titanium tetrachloride there can be produced the corresponding zirconium derivatives, e.g. zirconium tetra[monoacid mono (2-ethylhexyl) orthophosphate]; zirconium tri[monoacid mono (2-ethylhexyl) orthophosphate] mono[di(2-ethylhexyl orthophosphate]; zirconium bis[di(2-ethylhexyl) orthophosphate] bis [monoacid mono (2-ethylhexyl) orthophosphate]; and the like. Also the amine salts of the zirconium compounds can be prepared by simply substituting the stoichiometric equivalent quantity of the mixed reaction products as described hereinabove for zirconium in place of those of titanium in Example 2.

EXAMPLE 4

By following the procedure of Example 1 but substituting the stoichiometric equivalent quantity of other hydrocarbyl phosphates in place of the 2-ethylhexyl such as those of n-dodecyl, phenyl, benzyl, 3-butyltetradecyl, and 4-octylphenyl, the corresponding titanium compounds with the enumerated hydrocarbyl groups can be produced which, can be further reacted with various amines such as oleyl amine to produce the amine salts.

EXAMPLE 5

A mixture of phosphates (500 gm.) containing 445 gm. of (2-ethylhexyl) diacid orthophosphate and 55 gm. of di(2-ethylhexyl) monoacid orthophosphate were added by means of a separatory funnel over a period of seventeen minutes to 62 ml. of titanium tetrachloride dissolved in 500 ml. of heptane. After eight minutes the product was in the form of an orange colored gel. When all of the phosphate had been added heat was applied and nitrogen bubbled through the solution to carry off HCl. After 45 minutes all of the gel was dissolved. Heating was continued for three hours under reflux and then the solution allowed to stand overnight. The solution was then reheated and blown for two hours with nitrogen. The major reaction product was titanium tetra [monoacid mono (2-ethylhexyl) orthophosphate] and there were minor quantities of similar product wherein some of the phosphate groups contained two mono (2-ethylhexyl) groups. The solution was then neutralized with Alamine 11 (a commercial oleyl-amine). The neutralization point was determined by titratium of a sample dissolved in ASTM naphtha to the p-nitrophenol in methanol end point.

EXAMPLE 6

Mixed phosphates (75 gm.) containing 8.25 gm. of di(2-ethylhexyl) monoacid orthophosphate and 66.75 gm. of mono(2-ethylhexyl) diacid orthphosphate dissolved in 100 ml. of heptane were added by means of a separatory funnel to 9.45 ml. of titanium tetrachloride in 100 ml. of heptane. An orange colored gel formed during the first half of the addition and most of the HCl was formed at that time. As more phosphate was added the gel dissolved. After refluxing for fifteen minutes nitrogen was passed through the solution and the refluxing was continued for 2½ hours. Heat was cut off and nitrogen bubbling continued for thirty minutes. The reaction mixture having as its major reaction product titanium tetra mono (2-ethylhexyl) monoacid orthophosphate was brought to the neutral point with oleyl amine using p-nitrophenol indicator in order to produce the amine salt.

EXAMPLE 7

A mixture of phosphates (50 gm.) containing 89.5% of (2-ethylhexyl) diacid orthophosphate and 10.5% of di(2-ethylhexyl monoacid orthophosphate was dissolved in 100 ml. of substantially anhydrous heptane. Titanium tetrachloride (9.4 ml.) was added to the dry heptane and

the solution added to the dry hot phosphate solution with stirring. This was refluxed for 1½ hours with N_2 bubbling through the solution. The solution was then allowed to stand overnight and subsequently refluxed for an additional four hours. It was then cooled and transferred to a 250 ml. graduate. The product so produced was a mixture of titanium tetra [monoacid mono (2-ethylhexyl) orthophosphate]. This product was neutralized with diethanol amine to prepare a water soluble salt having as its main constituent titanium tetra [mono (diethanolammonium) mono (2-ethylhexyl) orthophosphate].

EXAMPLE 8

A mixture of phosphates (80.5 gm.) containing, by weight, about 89% of (2-ethylhexyl) diacid orthophosphate and about 11% of di(2-ethylhexyl) monoacid orthophosphate was dissolved in 100 ml. of heptane and added with stirring to 10.4 ml. of titanium tetrachloride and 100 ml. of heptane. The solution was refluxed for 3½ hours while blowing with nitrogen to remove HCl. The titanium [monoacid mono (2-ethylhexyl) orthophosphate]$_4$ produced was neutralized with 70.1 gm. of cocoamine, and the solvent removed under vacuum. The product was an amber colored viscous liquid with a slight haze. The yield was 153.8 gm.

EXAMPLE 9

A mixture of phosphates (50 gm.) containing about 44.5 gm. of (2-ethylhexyl) diacid orthophosphate and about 5.5 gm. of di(2-ethylhexyl) monoacid orthophosphate and 100 ml. of isooctane were added to 6.3 ml. of titanium tetrachloride in 75 ml. of isooctane. The solution was heated under reflux for 3.5 hours with nitrogen bubbling through the solution to remove hydrochloric acid. The solution contained a mixture of titanium tetra [monoacid mono (2-ethylhexyl) orthophosphate], together with other titanium orthophosphates having both 2-ethylhexyl and acid groups. The solution was neutralized with 34.2 gms. of oleyl-1, 3-propylene diamine to form the amine salts of the mixed titanium orthophosphates. The desired product was recovered by distilling off the solvent under reduced pressure.

EXAMPLE 10

Dissolved a mixture of orthophosphates composed of 44.5 gm. of mono (2-ethylhexyl) diacid orthophosphate and 5.5 gm. of di(2-ethylhexyl) monoacid orthophosphate in 100 ml. of isooctane and added it to 6.3 ml. (10.87 gm.) of titanium tetrachloride dissolved in 60 ml. of isooctane. Large amounts of HCl were evolved and a solid material formed which redissolved in the solvent. This solution was heated under reflux with nitrogen bubbling through the solution for 3.5 hours until only a trace of HCl could be detected with litmus in the gas stream. The solution contained a mixture of titanium phosphates including substantial quantities of titanium tetra [monoacid mono (2-ethylhexyl) orthophosphate] and a lesser quantity of titanium bis [di(2-ethylhexyl) orthophosphate] bis [mono(2-ethylhexyl) monoacid orthophosphate]. Di(2-ethylhexyl) amine (51.2 gm.) was added to the reacting mixture. The isooctane solution of the amine salt of the titanium hydrocarbyl acid phosphates was water washed and the isooctane removed under vacuum. The product was a clear yellow viscous liquid.

EXAMPLE 11

Following the procedure of Example 10 there was added 40.5 gm. of Primene 81R, a commercial form of tetra decyl amine to the reaction mixture and the solution washed twice with hot salt water, filtered to dry and the isooctane was removed under vacuum. The product was a clear almost colorless viscous liquid. The yield was 92.5 gms.

EXAMPLE 12

One hundred ml. of heptane were chilled and there was added to it 6.28 ml. (10.86 gm.) of titanium tetrachloride.

Fifty gm. of a cooled mixture of mono (2-ethylhexyl) diacid orthophosphate (89%) and di (2-ethylhexyl) monoacid orthophosphate (11%) in 50 ml. of heptane were added to the titanium tetrachloride solution. The beaker which contained the phosphate was rinsed with an additional 50 ml. of heptane. The solution was heated under reflux for four hours. The largest single constituent of the refluxed product was titanium tetra [monoacid mono (2-ethylhexyl) orthophosphate]. Fifty-eight and one-half grams of oleyl amine were added and the heptane removed under vacuum. The product was a clear yellow viscous liquid. The largest single constituent of the product was the oleyl amine salt of titanium tetra [monoacid mono (2-ethylhexyl) orthophosphate].

EXAMPLE 13

Mixed mono- and di-isooctyl acid phosphates (25.76 gm.) containing 14 gm. of mono(2-ethylhexyl) diacid orthophosphate and 11.33 gm. of di (2-ethylhexyl) monoacid orthophosphate were admixed with 25 ml. of heptane and the mixture was added to 3.794 gm. (2.2 ml.) of $TiCl_4$ in 50 ml. of heptane. The mixture was heated under reflux while blowing with N_2 for three hours. The solvent was removed under vacuum to give a white gelatinous material. This material was neutralized with 18.5 gm. of di (2-ethylhexyl) amine, diluted with pentane, and washed three times with water. It was then dried and pentane was removed.

EXAMPLE 14

Mono (2-ethylhexyl) diacid orthophosphate 84.0 gm. is dissolved in 200 ml. of toluene and added to 19 gm. of $TiCl_4$ dissolved in 150 ml. of toluene. The mixture was heated under reflux with nitrogen bubbling therethrough for four hours. The product in the reaction mixture is titanium 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 oleyl amine to produce titanium 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.

EXAMPLE 15

Following the procedure of Example 14 in the preparation of titanium tetra[monoacid mono (2-ethylhexyl) orthophosphate] there can be produced titanium tetra [(monodecyl monoacid orthophosphate)]; titanium tetra [mono (3-butyldodecyl) monoacid orthophosphate]; titanium tetra[(monophenyl monoacid orthophosphate)]; and titanium tetra[mono(4-octylphenyl) monoacid orthophosphate; by substituting for the mono (2-ethylhexyl) diacid orthophosphate the stoichiometric equivalent quantity respectively of monodecyl diacid orthophosphate; mono(3-butyldodecyl) diacid orthophosphate; monophenyl diacid orthophosphate; and mono (4-octylphenyl) diacid orthophosphate.

EXAMPLE 16

Titanium trichloride (15.3 gm.) in 100 ml. of benzene were admixed with 63 gm. of mono (2-ethylhexyl) diacid orthophosphate dissolved in 150 ml. of benzene. The mixture is heated at about 80° C. to form a solution containing titanium tri[mono(2-ethylhexyl) monoacid orthophosphate]. This titanium compound dissolved in the reaction mixture is neutralized with 30 gm. of hexylamine to prepare titanium tri[(monohexylammonium mono (2-ethylhexyl) phosphate].

EXAMPLE 17

This example together with Table 1 shows tests for icing inhibition in a spark ignition engine by the use of gasoline compositions containing additives of this invention. A single cylinder engine was operated at constant speed with inlet air conditions controlled to promote carburetor icing. Test conditions were chosen to give an increase in manifold vacuum of 2.5 inches of mercury in 20 seconds with the base fuel. A glass or clear plastic carburetor throttle body was used so that icing could be confirmed by visual inspection when desired. The base fuel was a mixture in equal parts by volume of isooctane and precipitation naphtha. Anti-icing was 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 an amine salt of this invention as compared to the base fuel without such an amine salt. The results of these tests wherein the time required for obtaining the specified vacuum is referred to as stall time are given in Table 1. In Table 1 additive A is titanium tetra[mono (oleylammonium) mono (2-ethylhexyl) orthophosphate]; additive B is titanium tetra[monoacid mono (2-ethylhexyl) orthophosphate] wherein the free acid groups were neutralized with N-oleyl-1,3-propylene diamine; and additive C is titanium tetra[mono(laurylammonium) mono (2-ethylhexyl) orthophosphate].

TABLE 1.—GASOLINE ANTI-ICING ACTIVITY

Additive	Concentration of Additive in p.p.m.	Percent Improvement in Stall Time Over Base Fuel
A	50	101
A	50	100
A	50	97
A	30	101
A	10	62
B	50	105
B	50	99
B	50	98
B	30	104
B	10	59
C	50	130

EXAMPLE 18

This example, together with Table 2 shows that gasoline compositions containing amine salts of this invention have carburetor detergency. A single cylinder engine, modified to greatly increase blowby, was operated at a part throttle, constant speed condition for 20 hours for each test. The engine was equipped with a blowby loop which returned blowby from the push rod cover to the air inlet side of the carburetor. The carburetor was disassembled after each test and visually merited by examining the top and bottom of the throttle plate and the venturi top and bottom. The gasoline compositions used in each test except for the base fuel which did not contain an additive contained 50 p.p.m. (parts per million) by weight of an additive of this invention. In Table 2, under the designation "Composition," the different letters refer to test base fuel containing: titanium tetra [monoacid mono (2-ethylhexyl) orthophosphate] wherein the free hydroxyl groups were neutralized with N-oleyl-1,3-propylene diamine and which is designated as A; titanium tetra [mono (oleylammonium) mono (2-ethylhexyl) orthophosphate] which is designated as B; titanium tetra [mono (laurylammonium) mono (2-ethylhexyl) orthophosphate] which is designated as C; titanium tetra [monoacid mono (2-ethylhexyl) orthophosphate] wherein the hydroxyl groups were neutralized with a mixture of primary branched chain alkylamines containing from 12 to 14 carbon atoms (Primene 81R). The results of these tests are shown in Table 2 wherein the merit rating of 10 represents clean whereas a merit rating of 0 represents black heavy deposits.

TABLE 2.—CARBURETOR DETERGENCY

Composition	Merit Rating	Percent Improvement Over Base Fuel
Base Fuel	3.8	
A	7.4	95
A	8.5	124
B	6.4	69
B	6.3	66
B	8.4	121
C	8.2	116
D	6.0	58

EXAMPLE 19

This example, taken with Table 3 shows that gasoline (base fuel) containing an amine salt of this invention improves the intake system cleanliness of internal combustion engines. In the cleanliness test, a single-cylinder engine, modified to greatly increase blowby, is cycled for 50 seconds at no load idle and 250 seconds at wide open throttle and 1050 r.p.m. until 150 hours are accumulated for each test composition. The engine is equipped with a blowby loop which returns blowby from the push rod cover to the air inlet side of the carburetor. The intake system is disassembled after each test and visually merit rated for cleanliness in the carburetor, intake manifold, and intake valve area. The results of a series of tests for intake system cleanliness appear in Table 3. Composition A in the table represents the base fuel containing 50 p.p.m. of titanium tetra [mono (oleylammonium) mono (2-ethylhexyl) orthophosphate]; Composition B represents the base fuel containing 50 p.p.m. of titanium tetra [mono (laurylammonium) mono (2-ethylhexyl) orthophosphate]; and Composition C represents the base fuel containing 50 p.p.m. of titanium tetra[monoacid mono (2-ethylhexyl) orthophosphate] wherein the acid groups are neutralized with a mixture of primary branched chain alkyl amines having from 12 to 14 carbon atoms.

TABLE 3.—INTAKE SYSTEM CLEANLINESS TEST

Composition	Merit Rating (Clean=100)	Percent Improvement Over Base Fuel
Base Fuel	36	
A	70	94
B	75	108
C	72	100
C	68	88

EXAMPLE 20

This example taken with Table 4 shows that the additives of this invention in base fuel (gasoline) reduce surface ignition of a spark ignition engine. A single-cylinder engine, equipped with an ionization gap to count flame fronts occurring before or after the normal flame, was operated at 1000 r.p.m. with the throttle cycled 50 seconds at idle and 250 seconds at wide open for 8 hours for each test. The average hourly surface ignition count for the last 4 hours of each test composition was compared to that of the base fuel without additive and reported on a percent reduction basis. The additive employed in these tests was titanium tetra[mono(oleylammonium) mono (2-ethylhexyl) orthophosphate]. The results of the tests are shown in Table 4.

TABLE 4.—SURFACE IGNITION SUPPRESSION

Concentration of additive in base fuel, p.p.m.:	Percent reduction from surface Ignition from base fuel
50	14
130	30
365	49

EXAMPLE 21

This example taken with Table 5 shows the reduction in octane requirement increase of base fuel (gasoline) containing an additive of this invention as compared to the base fuel without the additive. A V-8 passenger car engine using base fuel or base fuel plus an additive of this invention, modified to increase blowby, is cycled for 50 seconds at no load idle and 250 seconds at a medium load, moderate speed condition for 125 hours for each test. The engine is equipped with a blowby loop which returns blowby from the rocker arm cover to the air cleaner. The octane requirement of the engine at wide open throttle and 1000 r.p.m. is determined every 24 hours during the 125 hour period of the test. Octane requirements are plotted against test hours. The octane requirement increase for each test composition is calculated from the 100 hour requirement read from the curve minus the zero hour requirement. The results of a series of such tests are shown in Table 5 wherein the additives were used in a concentration of 50 p.p.m. in the base fuel and wherein: A designates titanium tetra[mono (oleylammonium) mono (2-ethylhexyl) orthophosphate]; B designates titanium tetra [monoacid mono(2-ethylhexyl) orthophosphate] wherein the acid groups were neutralized with N-oleyl-1,3-propylene diamine; and C designates mixed primary amines of branched chain alkyls having from 12 to 14 carbon atoms.

TABLE 5.—REDUCTION IN OCTANE REQUIREMENT INCREASE

Additive:	Percent reduction in octane requirement increase from base fuel
A	58
B	53
C	51

EXAMPLE 22

A gasoline composition affording rust inhibition, a reduction in octane requirement increase, protection against carburetor deposit build up, suppression of surface ignition, and inhibition of carburetor icing can be prepared by dissolving titanium tetra[mono(oleylammonium) mono (2-ethylhexyl) orthophosphate] in gasoline wherein the amine adduct is employed in a concentration of one pound for each 3,000 gallons of the composition.

EXAMPLE 23

Another suitable composition is that of a suitable base gasoline containing 100 p.p.m. by weight, of titanium tetra[mono (laurylammonium) mono (2-ethylhexyl) orthophosphate].

EXAMPLE 24

Another suitable composition can be prepared by dissolving two pounds of titanium bis[di(2-ethylhexyl) orthophosphate] bis[mono (oleylammonium) mono (2-ethylhexyl) orthophosphate] in 3,000 gallons of gasoline.

EXAMPLE 25

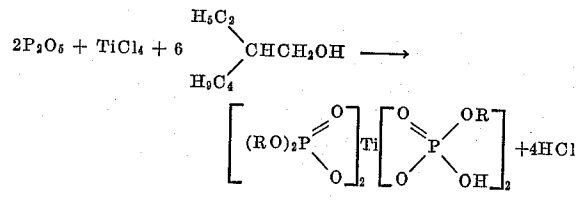
A suitable lubricating oil composition can be prepared by dissolving one pound of titanium bis[di(2-ethylhexyl) orthophosphate] bis[mono (oleylammonium) mono (2-ethylhexyl) orthophosphate] in 12 gallons of 200 neutral oil.

EXAMPLE 26

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

EXAMPLE 27

Titanium bis[di(2-ethylhexyl) orthophosphate] bis [monoacid mono (2-ethylhexyl) orthophosphate] is obtained from the reaction of 2 moles of phosphate pentoxide and one mole of titanium 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, there were added 400 ml. of anhydrous n-heptane and 71.0 g. (0.5 mole) of phosphorus pentoxide. With the stirrer going at a rate to insure a uniform dispersion, 47.4 g. (0.25 mole) of titanium tetrachloride was added next. Finally 215 g. (1.65 moles) of 2-ethyl-1-hexanol, contained in the pressure equalizing addition funnel, was run into the reaction vessel at a rate such that the temperature of the reactants did not rise above 60° C. When this step was completed, the solution was homogeneous. The reactants were then heated at 98°–103° C., and when evolution of hydrogen chloride moderated, dry air was passed through the solution to displace the acid gas more rapidly and to accelerate the reaction. When further evolution of hydrogen chloride was no longer observed, as revealed by Congo red indicator, the n-heptane and any unreacted octanol were removed by distillation in vacuo. The final temperature of the residual product in the reaction vessel was 175° at 25 mm. A very pale yellow syrupy product was obtained weighing 275 g. which is 99% of theory based on the metal halide. Inspection data were as follows:

Calculated formula weight for $TiC_{48}H_{104}P_4O_{16}$	1109.15
Calculated:	
Titanium, percent	4.32
Phosphorus, percent	11.17
Found:	
Titanium, percent	4.37; 4.30
Phosphorus, percent	11.24; 11.15
Refractive index, n_D^{20}	1.4750
Density, d_{20}	1.0836

Viscosity, SUS:	
At 100° F.	10,804
At 210° F.	665.6
ASTM color	1/2

What is claimed is:

1. An organic amine salt of a compound of the formula:

$$[(OH)(OR)OPO—]_nM[—OPO(OR)_2]_{n'}$$

wherein each R is a hydrocarbon group having from 1 to about 30 carbon atoms, M is a metal of Group IVB of the Periodic Table, (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 the amine has from 1 to about 30 carbon atoms.

2. A salt of claim 1 wherein the amine is aliphatic hydrocarbyl amine having from about 6 to about 24 carbon atoms and the total of (n) and (n') is 4.

3. A salt of claim 2 wherein each R is branched chain of from about 6 to about 22 carbon atoms.

4. A salt of claim 3 wherein the amine is an alkenylamine and R is alkyl.

5. A salt of claim 3 wherein the amine is a diamine and R is alkyl.

6. An organic amine salt of a compound of the formula:

$$[(OH)(OR)OPO]_nTi[—OPO(OR)_2]_{n'}$$

wherein each R is 2-ethylhexyl, (n) is an integer from 1 to 4, (n') is an integer from 0 to 3 and the amine has from 1 to about 30 carbon atoms.

7. A salt of claim 6 wherein the amine is aliphatic hydrocarbyl amine of from about 6 to about 24 carbon atoms and each of (n) and (n') is 2.

8. A salt of claim 6 wherein the amine is aliphatic hydrocarbyl amine of from about 6 to about 24 carbon atoms, (n) is 4 and (n') is 0.

References Cited

UNITED STATES PATENTS

2,346,155	4/1944	Denison et al.	260—429.3 X
3,231,347	1/1966	Revukas	260—429.3 X

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