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ORGANIC PHOSPHATE COMPLEXES

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The present invention relates to novel organic phosphate complexes and to processes for their preparation. In a more particular sense, it relates to corrosion-inhibiting coating compositions for metal comprising the aforesaid complexes.

The corrosion of metal articles is of obvious economic significance in many industrial applications and, as a consequence, the inhibition of such corrosion is a matter of prime consideration. It is particularly significant to users of steel and other ferrous alloys. The corrosion of such ferrous metal alloys is largely a matter of rust formation, which in turn involves the overall conversion of the free metal to its oxide.

The theory which best explains such oxidation of ferrous metal articles postulates the essential presence of both water and oxygen. Even minute traces of moisture are sufficient, according to this theory, to induce the dissolution of iron therein and the formation of ferrous hydroxide until the water becomes saturated with ferrous ions. The presence of oxygen causes the oxidation of the resulting ferrous hydroxide to ferric hydroxide, which then settles out of solution and is ultimately converted to ferric oxide or rust.

The above sequence of reactions can be prevented, or at least in large measure inhibited, by relatively impermeable coatings which have the effect of excluding moisture and/or oxygen from contact with the metal surface. Such coatings are often subjected to high humidity, corrosive atmospheres, and physical deformation and to the extent that these coatings are penetrated or otherwise harmed by such influences they become less effective for the desired purpose. A satisfactory corrosion-inhibiting coating then, must have the ability to resist weathering, high humidity, abrasion, deformation, and corrosive atmospheres such as salt-laden mist or fogs, air contaminated with industrial wastes, etc., so that a uniform protective film is maintained upon all or most of the metal surface.

Various derivatives of acid esters of phosphoric or phosphorothioic acids have been investigated by workers engaged in the task of providing improved protective coatings for metal. In U.S. Patent 2,080,299, for example, Benning et al. propose the treatment of ferrous metals with simple phosphate acid esters or their alkali metal and ammonium salts to prevent rusting. Somewhat similarly, Butler and Le Suer (U.S. Patents 2,861,907 and 2,820,723) find that salt-esters of certain phosphorothioic acids are effective in preventing or retarding the corrosion of metals.

Although such known derivatives of phosphoric and phosphorothioic acid have provided means for combating the corrosion of metals, they have not been completely satisfactory because of certain inherent shortcomings. The simple salt-esters of phosphoric acid are readily washed or abraded from a metallic surface and thus provide complete protection only in a favorable environment. The salt-esters of phosphorothioic acids, on the other hand, have the disadvantage, under certain conditions, of developing an objectionable odor reminiscent of hydrogen sulfide, particularly when a film of such a salt-ester comes in contact with water or humid atmospheres.

A further disadvantage of these known derivatives of phosphoric and phosphorothioic acids is that they form oily or tacky coatings which are not susceptible to the

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subsequent application of top-coats of siccative organic coating compositions such as paint, varnish, lacquer, enamel, and the like. Thus, their use has been limited to metal articles such as bulk castings, metal fasteners, firearm parts, iron cables, etc., which do not require a dry-film protective coating.

It is, therefore, a principal object of the present invention to provide novel organic phosphate complexes and processes for their preparation.

Another object is to provide corrosion-inhibiting coating compositions for metals, especially ferrous metals, which compositions comprise organic phosphate complexes.

A further object is to provide novel coating compositions for metals, which compositions are resistant to weathering, abrasion, deformation, high humidity and corrosive atmospheres.

A still further object is to provide means for improving the corrosion-inhibiting characteristics of known siccative organic coating compositions.

These and other objects of the invention are achieved by providing an organic phosphate complex prepared by the process which comprises the reaction of:

(A) one mole of a phosphorus-containing reagent selected from the group consisting of phosphorus pentoxide and phosphoric acids,

(B) from about 0.2 to about 12.5 moles of a copolymer of allyl alcohol and a styrene, and

(C) from about 0.1 to about 5 moles of a compound selected from the group consisting of alcohols, mercaptans, amines, amides, and thioamides,

at a temperature within the range from about 50° C. to about 300° C. In some instances, it is desirable to have present additionally in the process mass from about 0.1 to about 20 moles of an alkylphenol per mole of C present.

Thin films of the organic phosphate complexes of the present invention are remarkably effective in protecting metal surfaces, especially ferrous metal surfaces, against the ravages of corrosion. The complexes are also useful as ingredients in known siccative organic coating compositions such as paints, varnishes, lacquers, primers, synthetic resins, and enamels, to which compositions they impart enhanced corrosion-inhibiting characteristics. When used for the latter purpose, a minor proportion, generally from about 0.1 to about 25 percent, of an organic phosphate complex of this invention is blended with a major proportion, generally from about 99.9 to about 75 percent, of a siccative organic coating composition, all parts being by weight.

REAGENT A

As indicated above, the phosphorus-containing reagent A is selected from the group consisting of phosphorus pentoxide and a phosphoric acid. For reasons of convenience, economy, and reactivity in the process of this invention, phosphorus pentoxide is generally preferred. Where it is desired to employ phosphoric acid, any of the several available phosphoric acids such as polyphosphoric, orthophosphoric, metaphosphoric, or pyrophosphoric acid may be used either alone or in admixture as this reagent. It is also feasible to use mixtures of phosphorus pentoxide with one or more of these phosphoric acids. Phosphoric acid, if employed, will generally be the ordinary commercial 85 percent or 100 percent orthophosphoric acid, although more dilute acids containing at least about 25 percent H_3PO_4 are also usable.

REAGENT B

This reagent is a copolymer of 10 to 90 mole-percent of allyl alcohol with 90 to 10 mole-percent of a styrene. Especially useful for the purposes of this invention are copolymers prepared from approximately equimolar

amounts of the two monomers and having an average molecular weight within the range from about 500 to about 5000.

A particular preference is expressed for a copolymer of approximately equimolar amounts of allyl alcohol and styrene having an average molecular weight of about 1100-1150. Such a copolymer is available commercially under the trade designation, "Polyol X-450." Similar copolymers of lesser or greater average molecular weight are also available commercially, including one which has an average molecular weight of about 1580.

The term "a styrene" as used herein refers to styrene or any of various substituted styrenes such as halogen-substituted styrenes, hydrocarbon-substituted styrenes, alkoxy-styrenes, acyloxy-styrenes, nitro-styrenes, etc. Examples of such substituted styrenes include p-chloro-styrene, p-ethylstyrene, o-phenylstyrene, p-methoxystyrene, m-nitrostyrene, alpha-methylstyrene, and the like. In most instances, however, it is preferred to use styrene itself by reason of its low cost, commercial availability, and excellence as a raw material in the preparation of reagent B.

REAGENT C

The reagent is at least one compound selected from the group consisting of alcohols, mercaptans, amines, amides, and thioamides. In some instances, a single reagent may contain two or more of the desired groups. For example, an alkanolamine is both an alcohol and an amine. Likewise, a monothioglycol is both an alcohol and a mercaptan.

Alcohols useful as this reagent include both substituted and unsubstituted monohydric or polyhydric aliphatic or cycloaliphatic alcohols containing from 2 to 50 or more carbon atoms. Organic and/or inorganic substituents which may be present in the alcohols include principally aromatic or heterocyclic groups such as phenyl, alkyl-phenyl naphthyl, phenanthryl, pyridyl, etc., and other groups such as chloro, bromo, fluoro, nitro, nitroso, ether, ester, keto, sulfide, disulfide, etc. Illustrative of such alcohols are ethanol, n-propanol, isopropanol, n-butanol, isobutanol, 4-nitro-butanol-1, n-pentanol, neopentanol, commercial mixtures of primary amyl alcohols, n-hexyl alcohol, 4-methyl-pentanol-2, cyclohexanol, methylcyclohexanol, alphaterpineol, n-octanol, isooctanol, capryl alcohol, 3,5,5-trimethylhexanol, n-dodecanol, cetyl alcohol, oleyl alcohol, n-octadecanol, ceryl alcohol, alcohols derived from the oxidation of paraffin wax, tricosanol, triacontanol, hexatriacontanol, carnaubyl alcohol, ethylene glycol, propylene glycol, diethylene glycol, isobutylene glycol, hexamethylene glycol, 2-ethylhexanediol, 2-chloro-2-methylpropanol-1, 2-ethoxy-ethanol - 1, 2-butoxy-ethanol-1, mono-ethyl ether of diethylene glycol, ethylene glycol mono-oleate, glyceryl mono-stearate, glyceryl dipalmitate, 2-phenoxy-propandiol-1,3, benzyl alcohol, beta-phenethyl alcohol, allyl alcohol, 4-butenol-1, 2-alpha-pyridyl-ethanol-1, glycerol, 2-thioethoxy-ethanol - 1, pentaerythritol, sorbitol, sorbitol mono-oleate, mannitol, mannitol dilaurate, ethanolamine, diethanolamine, triethanolamine, propanolamine, commercial mixture of C₁₂-C₁₄ alcohols, beta-(isooctylphenoxy)ethanol, isooctylphenoxytetraethoxyethanol, 4-ketohexanol-1, 2,2'-dihydroxy-diethylsulfide, etc. In most instances, the alcohol will be an unsubstituted monohydric or polyhydric aliphatic alcohol containing from 2 to about 24 carbon atoms such as n-butanol, diethylene glycol, oleyl alcohol, hexylene glycol, pentaerythritol, isooctanol, n-dodecanol, etc.

Mercaptans useful as this reagent include the various substituted and unsubstituted mono- and poly-mercaptans containing from 2 to 30 or more carbon atoms. Substituents which may be present in the mercaptans include groups such as chloro, fluoro, bromo, nitro, nitroso, ether, sulfide, ester, keto, etc. Illustrative of mercaptans useful herein are ethyl, n-propyl, allyl, methallyl, n-butyl,

chlorobutyl, isooctyl, lauryl, cetyl, tricosyl, triacontyl, cyclohexyl, ethylcyclohexyl, phenyl, chlorophenyl, nitrophenyl, naphthyl, benzyl, chloro benzyl, etc., mercaptans; propandithiol-1,3, hexandithiol - 1,6, ethanol-1-thiol-2, propandiol-1,2-thiol-3, butyl thiolactate, diethyl mercaptosuccinate, 2-ethoxy-ethanthiol-1, 3-thioethoxy-propanthiol-1, octantrithiol-1,4,8, 2,3-diphenoxy-propanthiol-1, and 2-phenoxy-propanthiol-1,3. In most instances, the mercaptan will be an aliphatic mercaptan containing from about 2 to about 20 carbon atoms, especially an alkyl mercaptan such as tertiary-butyl mercaptan, tertiary-octyl mercaptan, lauryl mercaptan, etc.

Amines useful as this reagent include any of the various primary, secondary, and tertiary monoamines and polyamines containing from 2 to 30 or more carbon atoms, which amines may also contain substituents such as chloro, fluoro, bromo, nitro, nitroso, ether, ester, sulfide, etc. Examples of such amines include ethylamine, diethylamine, triethylamine, n-butylamine, isobutylamine, 6-chloro-n-hexylamine, tertiary-octyl primary amine, tertiary-dodecyl primary amine, tertiary-octadecyl primary amine, docosylamine, hexacosylamine, triacontylamine, hexatriacontylamine, aniline, alpha-naphthylamine, N-methylaniline, N,N-diethyl aniline, ring alkylated anilines such as ortho, meta, and para-toluidine, para-xylidine, ar-dodecyl aniline, etc., pyridine and alkylated pyridines, piperazine, aminoethyl-piperazine, quinoline, pyrimidine, morpholine, oxazines, thiazines, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, commercial mixtures of ethylene polyamines having an average molecular weight corresponding to tetraethylene pentamine, propylene diamine, hexamethylene diamine, N-hydroxyethyl-substituted mono-tertiary-dodecyl primary amine, commercial mixture of C₁₁-C₁₄ tertiary-alkyl primary amines having an average molecular weight of about 191, cyclohexylamine, dicyclohexylamine, allylamine, methallylamine, isooctenylamine, 2-butoxyethylamine, aminoethyl oleate, aminopropyl stearate, bis-(dimethylaminopropyl) amine, N-aminopropyl-octadecylamine, aminomethane, etc. In most instances, the amine will be an aliphatic amine of from 2 to about 20 carbon atoms which contains 1 to 5 amino groups such as tertiary-butyl primary amine, tertiary-dodecyl primary amine, triethylene tetraamine, tetraethylene pentamine, etc., or an aromatic amine such as pyridine, alpha-picoline, aniline, ar-dodecyl aniline, quinoline, and the like.

Also useful as reagent C are amides and thioamides having from 1 to 120 or more carbon atoms which may contain substituents such as chloro, bromo, fluoro, nitro, nitroso, ether, sulfide, ester, etc., as well as hydrocarbon substituents on the amido nitrogen atom. Examples of such amides and thioamides include urea and N-alkylated ureas, thiourea and N-alkylated thioureas, acetamide, thioacetamide, butyramide, caproamide, caprylamide, oleamide, stearamide, N,N-dimethyl stearamide, hexacosanoic acid amide, triacontanoic acid amide, carnaubic acid amide, 4-chloro butyramide, benzamide, thiobenzamide, N-lauryl benzamide, nitrobenzamide, the amides of petroleum naphthenic acids, cyclohexane carboxylic acid amides, alpha-naphthoic acid amide, adipamide, acrylamide, methacrylamide, sebacic acid amide, succinamide, polyisobutene-substituted succinamide wherein the polyisobutene substituent contains from 12 to 120 or more carbon atoms, commercial polyamides known as "Versamids" derived from high molecular weight aliphatic dicarboxylic acids and ethylene polyamines, orthophthaldiamide, ortho-phthalamid acid, lauryl orthophthalamate, succinamic acid, n-octyl succinamate, etc. In most instances, the amide will be an aliphatic amide. It is also possible and even desirable for certain applications to employ an acylated amide or thioamide, i.e., an imide, in lieu of or in partial replacement of the above-described amides and thioamides. Thus, it is contemplated that the terms amide and thioamide used in the

present specification and claims be inclusive of amides and thioimides. Examples of useful imides and thioamides are tertiary-dodecyl succinimide, ortho-phthalimide, N-dodecyl ortho-phthalimide, maleimide, tertiary-dodecyl thiosuccinimide, polyisobutene-substituted succinimide wherein the polyisobutene substituent contains from about 50 to about 120 carbon atoms, etc.

For certain applications, it has also been found that mixtures of any of the foregoing reagent C materials with an alkylphenol are useful in the process of this invention. When such mixtures are used, it is generally desirable to have present therein from about 0.1 to about 20 moles of an alkylphenol per mole of reagent C. Such alkylphenol may be a mono-alkyl or a poly-alkyl phenol. The alkyl groups may be of any size, ranging from methyl up to alkyl groups derived from olefin polymers having molecular weights as high as 50,000 or more. Preferably the alkylphenol is a mono-alkylphenol in which the alkyl group contains from 1 to about 30 carbon atoms, generally at least about 4 carbon atoms. Typical examples of useful alkylphenols include, e.g., ortho, meta, and para-cresols; ortho, meta, and para-ethylphenols; para-isopropylphenols, para-tertiary butylphenol, ortho-n-amyphenol, para-tertiary amyphenol, heptylphenol, diisobutylphenol, n-decylphenol, wax-alkylated alpha-naphthol, wax-alkylated phenol, and polyisobutene-substituted phenol in which the polyisobutene substituent contains from about 12 to about 76 carbon atoms. The alkylphenol may also contain substituent groups such as chloro, fluoro, nitro, nitroso, alkoxy, sulfide, ether, ester, etc. Also useful are polyhydric phenols such as alkylated, resorcinols, alkylated catechols, alkylated pyrogallols, and their substitution products.

The process for the formation of the organic phosphate complex of this invention may be carried out in any one of several ways. For example, reagents A, B, C, and, optionally, an alkylphenol and an inert solvent, may be placed in a reaction vessel and then heated and stirred at a temperature within the range from about 50° C. to about 300° C., preferably from about 80° C. to about 175° C., until the reaction is complete, which may require anywhere from 0.5 to 20 hours or more, depending on the particular reagents selected, the amount of such reagents, the reaction temperature employed, etc. In other instances, it is preferable to place reagent B and, optionally, an inert solvent in the reaction vessel, elevate the temperature to, say, 80° C., add reagents A, C, and, optionally, an alkylphenol, and then beat the whole in the manner set forth above. Still another method is to disperse reagent A in a suitable inert solvent, add reagents B, C, and, optionally, an alkylphenol, and then heat the whole in the described manner. It is necessary only that all the reagents be contacted within the desired temperature range, and whether the reagents be added simultaneously or successively, or the step of heating be carried out during or after the mixing of the reagents, appears to be of no consequence.

Generally it is most convenient to conduct the process of this invention in the presence of an inert, volatile solvent which serves to reduce the viscosity of the reaction mass. The solvent may remain in the final product, if desired, to facilitate its application to metal surfaces. Any of the solvents ordinarily employed in the paint and varnish industry may be used for the purpose such as benzene, xylene, toluene, mesitylene, cyclohexane, methylcyclohexane, aromatic petroleum spirits, chlorobenzene, trichloroethylene, ethylene dichloride, dioxane, turpentine, diisopropyl ether, and the like. Mixtures of one or more of the foregoing may also be used. In some instances, however, it is preferred to conduct the process in the absence of the solvent and then, optionally, to dilute the organic phosphate complex with the desired solvent or mixture of solvents prior to its application to a metal surface. This is generally the most advantageous and eco-

nomical procedure in instances where the organic phosphate complex is to be shipped to some distant point.

Generally, some water is evolved during the process of this invention. This is removed simply and conveniently by venting the reaction vessel to the atmosphere or, in cases where an inert solvent is employed, by azeotropic distillation or azeotropic reflux.

The precise chemical composition of the organic phosphate complexes of this invention is not known. It is believed, however, that the phosphorus-containing reagent phosphorylates the organic hydroxy compounds and any mercapto compounds present to form acid phosphate ester groups. Other reactions such as polymerization, salt formation, and/or etherification may also occur during the process and it is not intended that the theories presented herein be interpreted in any manner which would limit the scope of the invention, except as defined by the appended claims.

The following examples are presented to illustrate specific modes of carrying out the process of this invention. The "strong acid number" reported for the organic phosphate complex is determined according to ASTM procedure D974-55T, except that bromphenol blue is used as the end point indicator. Unless otherwise indicated, all parts and percentages are by weight.

Example 1

721 grams of xylene solvent and 575 grams (0.5 mole) of Polyol X-450 are introduced into a flask fitted with a reflux condenser and a side-arm water-trap. The whole is heated to 125° C. over a 20-minute period and then 89 grams (1.2 moles) of n-butanol and 57 grams (0.4 mole) of phosphorus pentoxide are added. Thereafter the reaction mass is refluxed for about 6 hours at 136° C. and 8 grams of water is observed to collect in the water-trap. The product in the flask, a 50 percent solution of the desired organic phosphate complex in xylene solvent, shows the following analyses.

Phosphorus, percent	1.69
Strong acid No.	32

Example 2

871 grams of xylene solvent and 575 grams (0.5 mole) of Polyol X-450 are introduced into a reaction vessel fitted with a reflux condenser and a side-arm water-trap. The whole is heated to 120° C. and then 239 grams (1.2 moles) of a commercial mixture of C₁₂-C₁₄ aliphatic alcohols and 57 grams (0.4 mole) of phosphorus pentoxide are added at 80-100° C. Thereafter, the reaction mass is refluxed for 5.5 hours at 145° C. while 11.5 grams of water is observed to collect in the side-arm water-trap. The product in the flask, a 50 percent solution of the desired organic phosphate complex in xylene, shows the following analyses.

Phosphorus, percent	1.44
Strong acid No.	26

Example 3

In a manner like set forth in Example 2, 919 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 287 grams (1.2 moles) of a commercial mixture of C₁₄-C₁₈ aliphatic alcohols, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period, 14.5 grams of water is observed to collect in the side-arm water-trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, shows the following analyses.

Phosphorus, percent	1.38
Strong acid No.	24

Example 4

In a manner like that set forth in Example 2, 954 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 322 grams (1.2 moles) of oleyl alcohol, and 57

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grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period, 14 grams of water is observed to collect in the side-arm water-trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, shows the following analyses.

Phosphorus, percent ----- 1.28
Strong acid No. ----- 23

Example 5

In a manner like that set forth in Example 2, 946 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 314 grams (1.2 moles) of a commercial mixture of higher fatty alcohols derived from sperm oil, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex of the present invention. During the reflux period, 12 grams of water is observed to collect in the side-arm water-trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is found to have the following analyses.

Phosphorus, percent ----- 1.35
Strong acid No. ----- 29

Example 6

In a manner like that that set forth in Example 2, 696 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 64 grams (6.0 mole) of diethylene glycol, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period, 10 grams of water is observed to collect in the side-arm water-trap. The product, a 50% solution of the desired organic phosphate complex in xylene, is filtered through cloth for the purpose of purification. The filtered product shows the following analyses.

Phosphorus, percent ----- 1.23
Strong acid No. ----- 30

Example 7

In a manner like that set forth in Example 2, 703 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 71 grams (0.6 mole) of hexylene glycol, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period 33 grams of water is observed to collect in the side-arm water-trap. The product, a 50 percent solution of a dark amber organic phosphate complex in xylene solvent, shows the following analyses.

Phosphorus, percent ----- 1.76
Strong acid No. ----- 38

Example 8

In a manner like that set forth in Example 2, 721 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 89 grams (0.6 mole) of 1,4-cyclohexane-dimethanol, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period, 12 grams of water collects in the side-arm water-trap. The product, a 50 percent solution of an amber organic phosphate complex in xylene solvent, is decanted from a small amount of a brown resin in the bottom of the reaction vessel. It shows the following analyses.

Phosphorus, percent ----- 0.77
Strong acid No. ----- 16

Example 9

702 grams of xylene solvent, 431 grams (0.375 mole) of Polyol X-450, and 17 grams (0.125 mole) of pentaerythritol are heated to 97° C. in a reaction vessel fitted with a reflux condenser and a side arm water trap. Thereafter, 197 grams (1.2 moles) of para-tertiary amylphenol and 57 grams (0.4 mole) of phosphorus pentoxide are added in the stated order to the reaction mass at 70-100° C. The whole is refluxed for 6.5 hours at 145° C. while 14

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grams of water is removed from the side-arm water-trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is decanted from a small amount of a brown resin in the bottom of the reaction vessel. The product shows the following analyses.

Phosphorous, percent ----- 1.32
Strong acid No. ----- 25

Example 10

In a manner like that set forth in Example 9, 576 grams of xylene solvent, 288 grams (0.25 mole) of Polyol X-450, 34 grams (0.25 mole) of pentaerythritol, 197 grams (1.2 moles) of para-tertiary amylphenol, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period, 10.5 grams of water is removed from the side-arm water-trap. The product, an amber, fluid, organic phosphate complex containing 50 percent xylene solvent, is decanted from a few grams of a hard resin which settles to the bottom of the reaction vessel. The product shows the following analyses.

Phosphorous, percent ----- 1.41
Strong acid No. ----- 27

Example 11

In a manner like that set forth in Example 9, 1890 grams of xylene solvent, 1150 grams (1.0 mole) of Polyol X-450, 34 grams (0.25 mole) of pentaerythritol, 492 grams (3 moles) of para-tertiary amylphenol, and 222 grams (1.56 moles) of phosphorous pentoxide react to form an organic phosphate complex of the present invention. During the reflux period, 31 grams of water is removed from the side-arm water-trap. The product, a 47.5 percent solution of the desired organic phosphate complex in xylene, is filtered for the purpose of purification. The filtered product shows the following analyses.

Phosphorus, percent ----- 2.0
Strong acid No. ----- 35

Example 12

In a manner like that set forth in Example 9, 1800 grams of xylene solvent, 1150 grams (1.0 mole) of Polyol X-450, 34 grams (0.25 mole) of pentaerythritol, 492 grams (3 moles) of para-tertiary amylphenol, and 142 grams (1.0 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period, 29 grams of water is collected in the side-arm water trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, shows the following analyses.

Phosphorus, percent ----- 1.41
Strong acid No. ----- 27

Example 13

1364 grams of xylene solvent and 575 grams (0.5 mole) of Polyol X-450 are introduced into a reaction vessel fitted with a reflux condenser and a side-arm water-trap. The whole is heated to 100-110° C. and then 732 grams (1.2 moles) of a commercial grade of isooctylphenoxy-polyethoxyethanol known under the trade designation "Triton X-100" and 57 grams (0.4 mole) of phosphorus pentoxide are introduced into the reaction vessel in the stated order at 74-100° C. The whole is refluxed for 6 hours at 143° C. while 8 grams of water is removed from the water-trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is an amber liquid which shows the following analyses.

Phosphorus, percent ----- 0.89
Strong acid No. ----- 17

Example 14

In a manner like that set forth in Example 13, 807 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 175 grams (1.2 moles) of tertiaryoctyl mercaptan, and 57 grams (0.4 mole) of phosphorus pentoxide react

to form an organic phosphate complex. During the reflux period, 11 grams of water is collected in the side-arm water-trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is an amber, somewhat viscous liquid which shows the following analyses.

Phosphorus, percent	1.48
Sulfur, percent	1.69
Strong acid No.	28

Example 15

In a manner like that set forth in Example 13, 720 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 88 grams (1.2 moles) of tertiarybutylamine, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex of this invention. During the reflux period, no water is evolved from the reaction mass. Upon cooling, the reaction mass deposits a small amount of white crystals, from which the liquid product is removed by decantation. 329 grams of isobutanol solvent is added to the decanted liquid product. The organic phosphate complex thus obtained is a clear yellow fluid containing 18.6 percent isobutanol solvent and 40.7 percent xylene solvent. It shows the following analyses.

Phosphorus, percent	0.49
Nitrogen, percent	0.40
Strong acid No.	5

Example 16

1078 grams of xylene solvent and 720 grams (0.625 mole) of Polyol X-450 are introduced into a reaction vessel fitted with a reflux condenser and a side-arm water-trap. The whole is heated to 80° C. and then 287 grams (1.5 moles) of a commercial mixture of C₁₁-C₁₄ tertiary-alkyl primary amines having an average molecular weight of 191 and 71 grams (0.5 mole) of phosphorus pentoxide are added in the stated order at 60-80° C. The whole is refluxed for 4 hours at 145° C. while 1.6 grams of water is observed to collect in the side-arm water-trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is a clear, yellow-orange viscous liquid showing the following analysis.

Phosphorus, percent	1.25
Nitrogen, percent	0.78
Strong acid No.	18

Example 17

In a manner like that set forth in Example 13, 1143 grams of xylene solvent, 720 grams (0.625 mole) of Polyol X-450, 352 grams (1.5 mole) of a technical grade of N-monohydroxyethyl-tertiary-dodecyl primary amine, and 71 grams (0.5 mole) of phosphorus pentoxide react to form an organic phosphate complex of the present invention. During the reflux period, 4.2 grams of water is observed to collect in the side-arm water-trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is a clear, yellow, somewhat viscous liquid showing the following analyses.

Phosphorus, percent	1.31
Nitrogen, percent	0.82
Strong acid No.	11

Example 18

845 grams of xylene solvent and 575 grams (0.5 mole) of Polyol X-450 are introduced into a reaction vessel fitted with a reflux condenser and a side-arm water-trap. The reaction mixture is heated to 90-120° C. and then 98 grams (0.6 mole) of para-tertiary amylphenol, 115 grams (0.6 mole) of a commercial mixture of C₁₁-C₁₄ tertiary-alkyl primary amines, and 57 grams (0.4 mole) of phosphorus pentoxide are added in the stated order at 77-93° C. The whole is refluxed for 6 hours at 144° C. No water is observed in the side-arm water-trap. The

product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is a light amber, viscous liquid showing the following analyses.

Phosphorus, percent	1.45
Nitrogen, percent	0.53
Strong acid No.	5

Example 19

In a manner like that set forth in Example 18, 837 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 148 grams (0.9 mole) of para-tertiary amylphenol, 57 grams (0.3 mole) of the commercial primary amine mixture described in Example 18, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex of the present invention. During the reflux period, 4 grams of water is collected in the side-arm water-trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene, is an amber, somewhat viscous liquid showing the following analyses.

Phosphorus, percent	1.48
Nitrogen, percent	0.26
Strong acid No.	16

Example 20

In a manner like that set forth in Example 13, 683 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 51 grams (0.24 average mole) of a commercial mixture of ethylene polyamines containing 33.4 percent nitrogen and having a composition corresponding to that of tetraethylene pentamine, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the 7-hour reflux period, 2 grams of water is observed to collect in the side-arm water-trap. The crude product is decanted from a small amount of an orange residue in the reaction vessel and the decanted liquid is blended with 155 grams of isobutanol solvent. The product, an organic phosphate complex which contains 10.2 percent isobutanol solvent and 44.9 percent xylene solvent, is a viscous liquid which shows the following analyses.

Phosphorus, percent	1.61
Nitrogen, percent	0.99
Strong acid No.	1 (basic)

Example 21

727 grams of xylene solvent and 575 grams (0.5 mole) of Polyol X-450 are introduced into a reaction vessel fitted with a reflux condenser and a side-arm water-trap. The whole is heated to 120° C. and then 95 grams (1.2 moles) of pyridine and 57 grams (0.4 mole) of phosphorus pentoxide are added in the stated order at 83-95° C. Thereafter, the reaction mass is refluxed for 5.25 hours, while 1 gram of water is collected in the side-arm water-trap. The desired organic phosphate complex is filtered from a tan crystalline by-product. The filtered product, which contains approximately 50 percent xylene solvent, is a clear yellow liquid showing the following analyses.

Phosphorus, percent	0.23
Nitrogen, percent	0.65

Example 22

In a manner like that set forth in Example 13, 744 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 112 grams (1.2 moles) of alphapicoline, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. The crude product is decanted from an amber residue in the reaction flask and filtered through sintered glass for purposes of purification. The filtered product, which contains approximately 50 percent xylene solvent, is a clear, yellow, somewhat viscous liquid showing the following analyses.

Phosphorus, percent	0.76
Nitrogen, percent	0.91
Strong acid No.	13

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Example 23

794 grams of xylene solvent and 546 grams (0.475 mole) of Polyol X-450 are introduced into a reaction vessel fitted with a reflux condenser and a side-arm water-trap. The whole is heated to 100° C. and then 194 grams (1.14 average moles) of a commercial mixture of lower alkylated pyridines consisting principally of xylidines and toluidines, and 54 grams (0.38 mole) of phosphorus pentoxide are added in the stated order at 52-70° C. Thereafter, the reaction mixture is refluxed for 5.5 hours and 3 grams of water is observed to collect in the side-arm water-trap. The crude product is decanted from a small amount of solid material on the bottom of the flask and filtered through cloth for purposes of purification. The filtered product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is a clear, dark-amber liquid showing the following analyses.

Phosphorus, percent	0.22
Nitrogen, percent	0.71
Strong acid No.	4

Example 24

In a manner like that set forth in Example 13, 777 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 145 grams (1.2 moles) of 2-methyl-5-ethyl-pyridine, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex of this invention. During the reflux period, 1.6 grams of water is collected in the side-arm water-trap. The product, which is decanted from a small amount of solid in the reaction vessel, contains approximately 50 percent xylene solvent and is a yellow, slightly cloudy fluid showing the following analyses.

Phosphorus, percent	0.3
Nitrogen, percent	0.41
Strong acid No.	5

Example 25

In a manner like that set forth in Example 18, 831 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 148 grams (0.9 mole) of paratertiary amylphenol, 51 grams (0.3 mole) of a commercial mixture of lower alkylated pyridines consisting principally of xylidines and toluidines, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex of the present invention. During the reflux period, 4 grams of water is observed to collect in the side-arm water-trap. The product is decanted from a small amount of a brown residue which collects in the bottom of the reaction vessel. The decanted material, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is an amber fluid having the following analyses.

Phosphorus, percent	0.98
Nitrogen, percent	0.16
Strong acid No.	16

Example 26

In a manner like that set forth in Example 13, 787 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 155 grams (1.2 moles) of quinoline, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period, 2 grams of water is observed in the side-arm water-trap. The product is decanted from a small amount of a brown residue which settles to the bottom of the reaction flask. The decanted material, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is an amber fluid showing the following analysis.

Phosphorus, percent	0.16
Nitrogen, percent	0.76
Strong acid No.	3

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Example 27

In manner like that set forth in Example 13, 946 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 314 grams (1.2 moles) of ar-dodecyl aniline, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period, 6 grams of water is collected in the side-arm water-trap. The product, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is a dark-amber, slightly viscous liquid showing the following analyses.

Phosphorus, percent	1.29
Nitrogen, percent	0.81
Strong acid No.	28

Example 28

In a manner like that set forth in Example 13, 969 grams of xylene solvent, 575 grams (0.5 mole) of Polyol X-450, 337 grams (1.2 moles) of a technical grade of oleamide, and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period, 5.5 grams of water is observed to collect in the side-arm water-trap. The crude product is filtered through cloth for purposes of purification. The filtrate, a 50 percent solution of the desired organic phosphate complex in xylene solvent, is an amber liquid showing the following analyses.

Phosphorus, percent	0.74
Nitrogen, percent	0.47
Strong acid No.	4

Example 29

965 grams of xylene solvent and 575 grams (0.5 mole) of Polyol X-450 are introduced into a reaction vessel fitted with a reflux condenser and a side-arm water-trap. The whole is heated to about 120° C. and 147 grams (0.9 mole) of para-tertiary amylphenol is added rapidly thereto at 71-82° C. While the whole is stirred at about 80° C., 186 grams of a polyamide derived from a high molecular weight aliphatic dicarboxylic acid and ethylene polyamines (known under the trade designation "Versamid-100") is added slowly over a period of about 2 hours at 60-74° C. Thereafter 57 grams (0.4 mole) of phosphorus pentoxide is added over a 5-minute period at 74-79° C. The reaction mass becomes very viscous, so an addition of 965 grams of xylene solvent is made to facilitate azeotropic reflux. The whole is then refluxed for 3 hours while 0.6 gram of water is collected in the side-arm water-trap. The product, a 33.3 percent solution of the desired organic phosphate complex in xylene solvent, shows the following analyses.

Phosphorus, percent	0.88
Nitrogen, percent	0.42
Strong acid No.	1 (basic)

Example 30

In a manner like that set forth in Example 29, 1100 grams of xylene solvent (2 portions of 834 and 266 grams, respectively), 575 grams (0.5 mole) of Polyol X-450, 147 grams (0.9 mole) of para-tertiary amylphenol, 55 grams of a polyamide derived from a high molecular weight aliphatic dicarboxylic acid and ethylene polyamines (known under the trade designation "Versamid-125"), and 57 grams (0.4 mole) of phosphorus pentoxide react to form an organic phosphate complex of the present invention. During the reflux period, 3.2 grams of water is collected in the side-arm water-trap. The product, a 43 percent solution of the desired organic phosphate complex in xylene solvent, is an amber, somewhat viscous liquid showing the following analyses.

Phosphorus, percent	1.26
Nitrogen, percent	0.37
Strong acid No.	9

Example 31

980 grams of xylene solvent and 575 grams (0.5 mole) of Polyol X-450 are introduced into a reaction vessel fitted with a reflux condenser and a side-arm water-trap. While the whole is heated to 120° C., 348 grams (0.6 mole) of N,N'-dioctadecyl-thiourea, and 57 grams (0.4 mole) of phosphorus pentoxide are added in the stated order at 103-120° C. Thereafter, the whole is refluxed for 6 hours while 2.5 grams of water is observed to collect in the side-arm water-trap. Upon cooling, the reaction mass is diluted with 1230 milliliters of isobutanol solvent and 500 milliliters of methyl isobutyl ketone solvent. For purposes of investigation, all the solvents were removed from the organic phosphate complex in this experiment. The solvent-free organic phosphate complex is a light-brown amorphous solid which shows the following analyses.

Phosphorus, percent	2.50
Nitrogen, percent	1.70
Strong acid No.	15

Example 32

In the same manner set forth in Example 13, 1,393 grams of xylene, 1,150 grams (1.0 mole) of Polyol X-450, 129 grams (0.68 mole) of a commercial mixture of C₁₁-C₁₄ tertiary-alkyl primary amines having an average molecular weight of about 191, and 114 grams (0.8 mole) of phosphorus pentoxide react to form an organic phosphate complex. During the reflux period, 7 grams of water is collected in the side-arm water-trap. The crude product is then stirred for 3 hours at 35° C. with 697 grams of isobutanol solvent.

The product, a solution of the desired organic phosphate complex containing 40% of xylene solvent and 20% of isobutanol solvent, is a clear, orange liquid showing the following analyses.

Phosphorus, percent	1.39
Nitrogen, percent	0.28
Strong acid No.	12

A number of laboratory and outdoor exposure tests were carried out to determine the utility of the herein-described organic phosphate complexes as protective coating compositions per se for metals, as primers to prepare a metal article to receive a top-coat of a siccative organic coating composition such as paint, varnish, lacquer, primers, synthetic resins, enamel, etc., and as improving agents in such siccative organic coating compositions. They are also useful as improving agents in water-base or emulsion paints such as synthetic latex paints derived from acrylic resins, polyvinyl alcohol resins, alkyd resins, etc., by emulsification thereof with water, as well as in water-soluble paints or primers derived from water-soluble alkyd resins, acrylic resins, and the like. The complexes of this invention may be applied to metal surfaces by any one of the methods ordinarily used in the paint and varnish industry such as brushing, spraying, dip-coating, flow-coating, roller-coating, and the like. The viscosity of the complex or the coating composition containing the complex may be adjusted for the particular method of application selected by adding a suitable amount of a solvent such as benzene, xylene, mesitylene, aromatic petroleum spirits, turpentine, or other appropriate solvents. The metal surface which has been thus coated is then dried either by exposure to air or by means of a baking procedure. A dry film thickness of the complex or the coating composition containing the same ranging from about 0.01 mil to about 4 mils, preferably 0.02-2 mils, is usually required to provide adequate protection for the metal surface. Coatings heavier than 4 mils can be used, if desired, but they normally contribute little in the way of additional protection. In some instances, it is desirable to admix the complex with a pigment such as titanium dioxide, chrome green, aluminum powder, carbon black, iron

oxide, or zinc chromate. In some instances, it is also desirable to include conventional improving agents such as pigment extenders, anti-skinning agents, driers, gloss agents, color stabilizers, etc.

Example A

A number of 4-inch by 8-inch panels of clean, 20-gauge cold-rolled SAE 1020 steel were dip-coated, respectively, with a good, commercial, air-dry clear alkyd primer and several complexes of this invention. Thereafter, each primed panel was air-dried for two days (dry film measured 0.1±0.01 mil), dip-coated with a commercial, white alkyd enamel, and baked in an oven for 20 minutes at 275° F. The film of baked enamel measured 1±0.1 mil.

The primed and top-coated panels were then subjected to a water immersion test. In this test, the panels are completely immersed for 16 hours in a water bath maintained at 160° F. Upon removal from the bath, each panel was rated for coating adhesion on a scale of 0 to 100, 100 representing a perfect panel free from blisters and/or flaking and 0 representing a completely blistered and/or flaked panel.

The results obtained in this test are set forth in Table I.

TABLE I.—WATER IMMERSION TEST

Primer used under enamel	Coating adhesion value
top-coat:	
Commercial alkyd primer (control)	44
Product of Example 14	100
Product of Example 1	85
Product of Example 32	100

It will be noted that the complexes of this invention were superior to a known primer in improving the adhesion of an enamel to a ferrous surface.

Example B

A number of primed and top-coated panels were prepared in the manner set forth in Example A and then subjected to the water immersion test described in that example. Upon removal from the bath, each panel was "cross-hatched" with a pointed steel instrument by making eleven parallel, one-inch long scribes spaced 3/32-inch apart and a similar number of intersecting scribes at right angles thereto. Adhesive cellophane tape was then applied to the scribed area and removed. The scribed area was rated for coating adhesion on a scale of 0 to 10, 10 representing a perfect panel showing no loss of the coating and 0 representing a panel which lost all of the coating in the cross-hatched area.

The results observed in this test are shown in Table II.

TABLE II.—CROSS-HATCH ADHESION TEST
(AFTER WATER IMMERSION)

Primer used under enamel	Cross-hatch adhesion value
top-coat:	
Commercial alkyd primer (control)	0
Product of Example 14	2
Product of Example 1	9
Product of Example 32	10

Again, the complexes of this invention were more effective than a known primer in promoting the adhesion of an enamel to a ferrous surface.

Example C

A number of 4-inch by 8-inch panels of clean, 20-gauge cold-rolled SAE 1020 steel were primed, respectively, with a commercial, clear alkyd primer and several complexes of this invention and allowed to air-dry for two days. The film thickness on each panel was found to be 0.1±0.01 mil.

The primed panels were then placed in a rack at a 45° angle and stored outdoors in the Great Lakes region for

one week. The condition of the panels after outdoor exposure is described in Table III.

TABLE III.—OUTDOOR EXPOSURE TEST (ONE WEEK)

Primer coat on panel:	Inspector's remarks	
Commercial alkyd primer (control) -----	Heavy rusting on edges; scattered rust spots on weather face.	5
Product of Example 14 --	No edge rust; a few rust spots on weather face.	10
Product of Example 1 ---	No rust; weather face slightly discolored.	
Product of Example 32 --	No edge rust; a few rust spots on weather face.	15

It will be noted that the complexes of this invention are useful per se as clear film primers for metal surfaces. They are more effective for this purpose than a known, clear film primer.

Example D

A number of primed and top-coated steel panels were prepared in the same manner set forth in Example A, except that a commercial, amine-modified alkyd white enamel was used as the top-coat material and the baking schedule was 20 minutes at 400° F.

The primed and top-coated panels were subjected to a salt fog corrosion test for 100 hours. The apparatus used for this test is described in ASTM procedure B 117-57T. It consists of a chamber in which a mist or fog of 5 percent aqueous sodium chloride solution is maintained in contact with the test panels at 95°±2° F. The panels in this instance were removed from the chamber after 100 hours, washed with water, and scraped vigorously with a putty knife to remove any coating which had loosened. Each panel was inspected to determine the percent of the total area thereof which was still covered with an adherent coating (reported as "percent of coating adhered"). The results are shown in Table IV.

TABLE IV.—SALT FOG CORROSION TEST, 100 HOURS

Primer used under enamel top-coat:	Percent of coating adhered	
Commercial alkyd primer (control) -----	37	45
Product of Example 14 -----	82	
Product of Example 1 -----	68	
Product of Example 32 -----	48	50

It will be noted that the complexes of this invention were more effective than a known primer in improving the adhesion of an enamel top-coat to a metal surface in a highly corrosive environment.

Example E

A commercial white enamel was milled from 400.3 parts of pigment grade titanium dioxide, 713.9 parts of a commercial alkyd resin (60% non-volatiles), 1.5 parts of a commercial cobalt naphthenate drier (6% cobalt content), 232.8 parts of aromatic petroleum spirits, and 22.5 parts of varnishmaker's naphtha.

A similar group of enamels was compounded, differing only in that 7 percent of the alkyd resin (i.e., 50 parts thereof) was replaced, respectively, by 50 parts of a number of different complexes of this invention.

Steel panels of the type previously described were dipped, respectively, in the commercial white enamel and the experimental enamels containing organic phosphate complexes of this invention, then baked for 20 minutes at 275° F. The top-coated panels were subjected to the water immersion test described in Example A. Another similarly prepared set of panels was subjected to the cross-hatch adhesion test described in Example B. The results obtained in each of the tests are shown in Table V.

TABLE V.—WATER IMMERSION AND CROSS-HATCH ADHESION TESTS

Enamel Used To Provide Coating For Steel Panel	Water Immersion Adhesion Value	Cross-Hatch Adhesion Value
Commercial white enamel (control) -----	18	0
Enamel containing the product of Example 20 -----	100	10
Enamel containing the product of Example 14 -----	53	1
Enamel containing the product of Example 1 -----	100	10
Enamel containing the product of Example 2 -----	87	9
Enamel containing the product of Example 6 -----	66	10
Enamel containing the product of Example 32 -----	77	10
Enamel containing the product of Example 30 -----	67	4

It will be noted that the complexes of this invention are effective as additives in a known siccative organic coating composition for the purpose of improving adhesion.

Example F

A group of steel panels prepared in the same manner set forth in Example E was subjected to the Olsen cup test. The test, which measures the adhesion of a coating composition to a metal surface under severe deformation conditions, consists of a device in which the coated test panel is securely clamped and then deformed. Access is provided to the panel through a one-inch diameter circular opening. Through this opening, a 7/8-inch diameter rounded cylindrical piston is forced against the panel until the resulting dimple ruptures. The panel is then removed and pressure-sensitive tape is applied to the convex surface of the dimple. After removal of the tape, the convex surface of the dimple is rated on a scale of 0 to 5, 5 indicating perfect adhesion and 0 indicating a complete loss of the coating composition (i.e., no adhesion).

The results obtained in this test are shown in Table VI.

TABLE VI.—OLSEN CUP TEST

Enamel used to provide coating for steel panel:	Olsen adhesion value
Commercial white enamel (control) -----	3
Enamel containing the product of Example 20 --	5
Enamel containing the product of Example 14 --	4
Enamel containing the product of Example 1 --	5
Enamel containing the product of Example 2 ---	4
Enamel containing the product of Example 6 ---	4
Enamel containing the product of Example 32 --	4
Enamel containing the product of Example 30 --	4

It will be noted that the complexes of this invention are effective as additives in a known siccative organic coating composition for the purpose of improving adhesion under severe conditions of deformation.

In addition to their utility as protective coating materials for ferrous metals, the organic phosphate complexes of this invention are useful in protecting non-ferrous metals and alloys thereof such as aluminum, magnesium, copper, brass, bronze, white metal, etc., against corrosion. They are also useful as protective coating materials on galvanized ferrous surfaces, on plated metal surfaces such as copper-plated, nickel-plated, and cadmium-plated ferrous surfaces, and on phosphated metal surfaces. They are also useful as protective coating materials on "chromated" aluminum or "chromated" zinc surfaces, i.e., aluminum or zinc surfaces which have been treated with an aqueous solution of chromic acid and/or a derivative thereof such as a metal chromate or dichromate, an amine chromate, ammonium chromate, etc. Particularly fine results are obtained when the coating compositions of the present invention are applied over a metal surface which has been phosphated by

means of a novel aqueous phosphating solution containing as essential ingredients zinc ion, phosphate ion, nitrate ion, and a cation selected from the group consisting of lithium, beryllium, magnesium, calcium, strontium, cadmium, and barium. Such phosphating solutions, which provide a dense, adherent, micro-crystalline or amorphous phosphate coating upon the metal substrate, are described in detail in co-pending U.S. application, Ser. No. 373,449, filed August 10, 1953, now Patent No. 3,090,709, issued May 21, 1963. It is intended that the entire disclosure of Ser. No. 373,449 be incorporated herein by reference.

What is claimed is:

1. An organic phosphate complex prepared by the process which comprises the reaction of a mixture consisting essentially of:

(A) one mole of a phosphorus-containing reagent selected from the group consisting of phosphorus pentoxide and phosphoric acids,

(B) from about 0.2 to about 12.5 moles of a copolymer of allyl alcohol and a styrene, and

(C) from about 0.1 to about 5 moles of a compound other than an epoxy aryl ether, said compound being selected from the group consisting of alcohols, mercaptans, amines, amides, and thioamides,

at a temperature within the range from about 50° C. to about 300° C.

2. An organic phosphate complex prepared by the process which comprises the reaction of a mixture consisting essentially of:

(A) one mole of a phosphorus-containing reagent selected from the group consisting of phosphorus pentoxide and phosphoric acids,

(B) from about 0.2 to about 12.5 moles of a copolymer of allyl alcohol and a styrene,

(C) from about 0.1 to about 5 moles of a compound other than an epoxy aryl ether, said compound being selected from the group consisting of alcohols, mercaptans, amines, amides, and thioamides, and

(D) from about 0.1 to about 20 moles of an alkylphenol per mole of (C),

at a temperature within the range from about 50° C. to about 300° C.

3. A complex in accordance with claim 1 characterized further in that the phosphorus-containing reagent of (A) is phosphorus pentoxide.

4. A complex in accordance with claim 1 characterized further in that the copolymer of (B) is a copolymer of about equimolar amounts of allyl alcohol and styrene and has an average molecular weight in the range from about 500 to about 5,000.

5. A complex in accordance with claim 1 characterized further in that the compound of (C) is a monohydric alcohol.

6. A complex in accordance with claim 3 characterized further in that the copolymer of (B) is a copolymer of about equimolar amounts of allyl alcohol and styrene and has an average molecular weight in the range from about 1100 to about 1150, and the compound of (C) is n-butanol.

7. A complex in accordance with claim 1 characterized further in that the compound of (C) is a polyhydric alcohol.

8. A complex in accordance with claim 3 characterized further in that the copolymer of (B) is a copolymer of about equimolar amounts of allyl alcohol and styrene and has an average molecular weight in the range from about 1100 to about 1150, and the compound of (C) is diethylene glycol.

9. A complex in accordance with claim 1 characterized further in that the compound of (C) is an aliphatic mercaptan.

10. A complex in accordance with claim 3 characterized further in that the copolymer of (B) is a copolymer of about equimolar amounts of allyl alcohol and styrene and has an average molecular weight in the range from about 1100 to about 1150, and the compound of (C) is tertiary-octyl mercaptan.

11. A complex in accordance with claim 1 characterized further in that the compound of (C) is an aliphatic amine.

12. A complex in accordance with claim 3 characterized further in that the copolymer of (B) is a copolymer of about equimolar amounts of allyl alcohol and styrene and has an average molecular weight in the range from about 1100 to about 1150, and the compound of (C) is a mixture of C₁₁ to C₁₄ tertiary-alkyl primary amines having an average molecular weight of about 191.

13. A complex in accordance with claim 1 characterized further in that the compound of (C) is an aromatic amine.

14. A complex in accordance with claim 1 characterized further in that the compound of (C) is an aliphatic amide.

15. A metal article which has been protected against corrosion by applying thereto a film comprising the complex of claim 1.

16. A metal article which has been protected against corrosion by applying thereto a film which comprises a major proportion of a siccative organic coating composition and a minor proportion of the complex of claim 1.

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