

1

3,241,983

CORROSION-PROOFING COMPOSITION

John Bretz, Cleveland, Ohio, assignor to The Lubrizol Corporation, Wickliffe, Ohio, a corporation of Ohio
No Drawing. Filed Jan. 22, 1963, Ser. No. 253,033
14 Claims. (Cl. 106—14)

The present invention relates, as indicated, to a corrosion-proofing composition, which composition is adapted to form a protective coating on metal articles. In a more particular sense, it relates to a method for protecting metal articles, especially ferrous metal articles, against corrosion.

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 oxides.

The theory which best explains such oxidation of ferrous metal surfaces 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 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 exposed to high humidity, corrosive atmospheres, etc., and to the extent that these coatings are penetrated or otherwise harmed by such influences they become ineffective for the desired purpose. It is also important that such coatings adhere tightly to the metal surface and resist flaking, crazing, blistering, powdering, and other forms of loss of adhesion. A satisfactory corrosion-proofing coating, then, must have the ability to resist weathering, high humidity, 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 protective coatings for metals. In U.S. Patent 2,080,299, for example, Benning et al propose the treatment of ferrous metals with phosphate acid esters or their alkali metal or ammonium salts to prevent rusting. Somewhat similarly, Butler and LeSuer (U.S. Patents 2,861,907 and 2,820,723) find that salt-esters of complex phosphorothioic acids are effective in preventing or retarding the corrosion of metals.

Although such known derivatives of phosphoric and phosphorothioic acids 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 metal 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.

2

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 subsequent application of top-coats of siccative organic coating compositions such as paint, varnish, lacquer, enamel, primers, synthetic resins, 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 a novel, liquid corrosion-proofing composition.

Another object is to provide a method for inhibiting the corrosion of metal articles, especially ferrous metal articles.

A further object is to improve the adhesion of known, siccative organic coating compositions to metal articles.

A still further object is to improve the corrosion-proofing characteristics of known, siccative organic coating compositions.

These and other objects of the invention are realized by the provision of a liquid corrosion-proofing composition adapted to form a protective coating on metal articles which comprises the combination of:

(A) the product obtained by mixing one mole of at least one aliphatic amine containing at least about 6 carbon atoms with from about 0.25 to about 2 moles of aqueous chromic acid and heating the mixture to remove substantially all water present, and

(B) an acylated 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 5 moles of a copolymer of allyl alcohol and a styrene,

(c) from about 0.5 to about 5 moles of an alkylphenol, and

(d) from about 0.5 to about 4 moles per mole of (b) employed of an unsaturated aliphatic carboxylic acid compound selected from the group consisting of high molecular weight unsaturated aliphatic carboxylic acids containing at least about 12 carbon atoms and esters of such acids,

at a temperature within the range from about 50° C. to about 300° C. for about 0.5 to about 30 hours.

In most instances, the corrosion-proofing composition of this invention will comprise from about 0.05 to about 20 parts by weight of (A) per part of (B).

Thin films of the corrosion-proofing composition of the present invention are remarkably effective in protecting metal articles, especially ferrous metal articles, against the ravages of corrosion. If desired, a top-coat of a known siccative organic coating composition may be subsequently applied so as to provide additional protection, decorative effects, etc.

The corrosion-proofing compositions of this invention are also useful as ingredients in known, siccative organic coating compositions such as solvent-based paints, varnishes, lacquers, primers, synthetic resins, and enamels, to which compositions they impart enhanced corrosion-inhibiting characteristics. The siccative organic coating composition may also be an aqueous base or emulsion paint such as synthetic latex paints derived from acrylic resins, polyvinyl alcohol resins, alkyd resins, etc., by emulsification thereof with water, as well as water-soluble paints derived from water-soluble alkyd resins, acrylic resins, and the like. Such siccative organic coating compositions may contain conventional improving

agents such as pigment extenders, anti-skinning agents, driers, gloss agents, color stabilizers, etc.

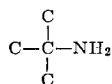
When used for this purpose, i.e., to improve known coating compositions, a minor proportion, generally from about 0.1 to about 25 percent, of the corrosion-proofing composition of this invention is blended with a major proportion, generally from about 99.9 to about 75 percent, of a siccative organic coating composition, all parts being by weight.

COMPONENT A

This component, as indicated, is prepared by mixing one mole of at least one aliphatic amine containing at least about 6 carbon atoms with from about 0.25 to about 2 moles of aqueous chromic acid and heating the mixture to remove substantially all water present. The product of this reaction is believed to be principally an amine salt of chromic acid, although other materials such as amine dichromates, amine oxidation products (chromic acid is known to be a strong oxidizing agent), etc., may be formed and contribute substantially to its properties. In most instances, it is preferred to use amounts of the amine and the aqueous chromic acid within the range from the stoichiometric amounts for the amine acid chromate (equimolar proportions of the amine and aqueous chromic acid) to the stoichiometric amounts for the normal amine chromate (one mole of the amine and 0.5 mole of aqueous chromic acid). It is also desirable in some instances to use two or more products derived from reactions involving different amounts of the amine and the aqueous chromic acid. Of course, proportions of the amine and aqueous chromic acid outside the scope of the broad range of 1 mole of the amine and from about 0.25 to about 2 moles of aqueous chromic acid may be employed, if desired, although the products of such reaction will contain excess amine or excess chromic acid and are, therefore, uneconomical and not preferred for the purposes of this invention.

Amines useful for the preparation of Component A include any of the various aliphatic primary, secondary, and tertiary monoamines and polyamines containing a total of from 6 to about 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 triethylamine, di-n-butylamine, di-isobutylamine, tri-isobutylamine, 6-chloro-n-hexylamine, 3-amino-n-heptane, 2-ethylhexylamine, tertiary-octyl primary amine, 3,5,5-trimethyl-hexylamine, n-decylamine, di-n-decylamine, tri-n-decylamine, tertiary-dodecyl primary amine, tertiary-octadecyl primary amine, cetylamine, n-octadecylamine, eicosylamine, docosylamine, hexacosylamine, triacontylamine, hexatriacontylamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, dicyclohexylamine, isoocetylamine, 2-butoxy-ethylamine, aminoethyl oleate, aminopropyl stearate, bis-(dimethylaminopropyl)amine, n-aminopropyl-octadecylamine, aminomenthane, etc.

A particular preference is expressed for monoalkyl primary amines conforming to the structure RNH_2 wherein R is an alkyl radical. Examples of such monoalkyl primary amines include n-hexylamine, 2-ethylhexylamine, laurylamine, cetylamine, and tertiary-alkyl primary amines. The tertiary-alkyl primary amines referred to conform to the characterizing structure



wherein a tertiary carbon atom, i.e., one devoid of hydrogen atoms, is bonded to a primary amino radical, i.e., $-\text{NH}_2$. Such tertiary-alkyl primary amines should contain at least about 6 and generally not more than about 30 carbon atoms in the tertiary-alkyl substituent. In most instances, the tertiary-alkyl substituent will contain from about 10 to about 24 carbon atoms. Specific examples

of tertiary-alkyl primary amines useful for the purposes of this invention include tertiary-octyl primary amine, tertiary-decyl primary amine, tertiary-dodecyl primary amine, tertiary-tetradecyl primary amine, tertiary-hexadecyl primary amine, tertiary-heptadecyl primary amine, tertiary-octadecyl primary amine, tertiary-eicosyl primary amine, tertiary-docosyl primary amine, tertiary-tetracosyl primary amine, tertiary-triacontyl primary amine, etc. It is not necessary to use a single tertiary-alkyl primary amine. In fact, it is generally more convenient to use a commercial mixture of such amines wherein the tertiary-alkyl substituent present contains from about 10 to about 24 carbon atoms. A typical mixture of such commercial tertiary-alkyl primary amines, for example, consists of tertiary-alkyl primary amines containing from about 12 to about 15 carbon atoms, said mixture averaging about 12 carbon atoms per amine molecule. This mixture, available commercially under the trade designation "Primine 81R," contains about 85 percent of tertiary-dodecyl primary amine, about 10 percent of tertiary-pentadecyl amine, and less than about 5 percent of amines having less than 12 or more than 15 carbon atoms. Another mixture of commercial tertiary-alkyl primary amines suitable for the purposes of the present invention consists of tertiary-alkyl primary amines having from about 18 to about 24 carbon atoms and averaging about 20 carbon atoms per amine molecule. This mixture of tertiary-alkyl primary amines contains about 40 percent of tertiary-octadecyl primary amine, about 30 percent of tertiary-eicosyl primary amine, about 15 percent of tertiary-docosyl primary amine, about 10 percent of tertiary-tetracosyl amine, and about 5 percent of amines outside the C_{18} to C_{24} range.

Tertiary-alkyl primary amine mixtures such as described above can be prepared by methods within the knowledge of those skilled in the art. For example, such mixtures may be prepared from polypropylene or polybutene fractions or mixtures thereof. Thus, a selected polymer fraction composed of mixed polyolefins within the desired molecular weight range can be converted to the corresponding tertiary-alkyl primary amines as follows. The selected polyolefin fraction is first hydrated by means of sulfuric acid and water to convert it to the corresponding alcohols. The alcohol mixture is then converted to alkyl chloride by the reaction with dry hydrogen chloride. Finally, the alkyl chloride mixture is condensed under pressure with ammonia to produce the desired tertiary-alkyl primary amine mixture. Specific method of preparing tertiary-alkyl primary amines are described in the Journal of Organic Chemistry, vol. 20 (1955), beginning on page 295.

The aqueous chromic acid employed in the preparation of Component A will range from a saturated aqueous solution of chromic acid (contains about 74 percent of H_2CrO_4) to a dilute aqueous solution containing as little as 5 or 10 percent of H_2CrO_4 . For the most convenient and economical operation, it is generally preferred to use saturated or near-saturated aqueous solutions of chromic acid.

The conditions of time and temperature employed for the reaction of the amine and the aqueous chromic acid are not critical. It is only necessary that the two reactants be reacted under conditions such that substantially all of the water present be removed. Thus, for example, the reactants may be maintained at the boiling point until water ceases to distill from the reaction mass. A more rapid and economical removal of water may be effected by heating the reaction mass at a temperature of, say 60-100° C. under reduced pressure until no more water distills. In any event, the process is carried out until water no longer distills from the reaction vessel. If desired, the somewhat viscous product may be diluted with a solvent such as benzene, toluene, xylene, aromatic petroleum spirits, naphtha, etc., to facilitate handling.

The following examples are submitted to illustrate specific modes of preparing Component A. They are pre-

sented for purposes of illustration only and are not to be construed as limiting the scope of the present invention, except as the latter is defined by the appended claims.

Example 1

122 parts of water and 162 parts of CrO_3 are mixed at 25–40° C. to yield a concentrated aqueous solution of chromic acid. 620 parts of a commercial mixture of C_{12} – C_{15} tertiary-alkyl primary amines (2 moles of amine per mole of aqueous chromic acid) is added to the aqueous chromic acid solution over a period of 0.5 hour. An exothermic reaction carries the temperature from 25° C. to about 80° C. The whole is then stirred for about 2 hours at 80–100° C. and then the pressure is reduced to about 50 mm. Hg to remove substantially all of the water present. 47 parts of organic distillate is separated from the aqueous distillate and recharged to the reaction vessel. To facilitate handling the somewhat viscous product, 90 parts of aromatic petroleum spirits is added. The product, a 90 percent solution of the active chemical in aromatic petroleum spirits, shows the following analyses:

Percent chromium	9.5
Percent nitrogen	5.1

Example 2

180 parts of water and 238 parts of CrO_3 are mixed at 25–40° C. to yield a concentrated aqueous solution of chromic acid. 620 parts of a commercial mixture of C_{12} – C_{15} tertiary-alkyl primary amines (1.36 moles of amine per mole of aqueous chromic acid) is added to the aqueous chromic acid over a period of about 0.5 hour. Thereafter, the whole is processed in the same manner set forth in Example 1 above. The product, a 90 percent solution of the active chemical in aromatic petroleum spirits, shows the following analyses:

Percent chromium	12.6
Percent nitrogen	4.5

Example 3

200 grams of CrO_3 is mixed with 200 grams of water to form a concentrated aqueous solution of chromic acid. Such solution is then added to 764 grams of a commercial mixture of C_{12} – C_{15} tertiary-alkyl primary amines (2 moles of amine per mole of aqueous chromic acid) over a period of 0.7 hour. An exothermic reaction causes the temperature to rise to about 37° C. One liter of benzene solvent is added to the reaction vessel and the contents are refluxed, using a side-arm water trap to remove water. After substantially all of the water is removed, the benzene solvent is removed at 87° C./50 mm. Hg. The product, a brown viscous liquid, shows the following analyses:

Percent chromium	11.0
Percent nitrogen	5.7

Example 4

In the same manner set forth in Example 3, 800 grams of concentrated aqueous chromic acid (from 400 grams of CrO_3 and 400 grams of water) and 764 grams of a commercial mixture of C_{12} – C_{15} tertiary-alkyl primary amines (equimolar proportions of the amine and the aqueous chromic acid) are processed to yield a product useful for the purposes of this invention. The product, a dark brown viscous liquid, shows the following analysis:

Percent chromium	17.1
Percent nitrogen	4.46

Example 5

In the same manner set forth in Example 3, 200 grams of concentrated aqueous chromic acid (from 100 grams each of CrO_3 and water) and 573 grams of a commercial mixture of C_{12} – C_{15} tertiary-alkyl primary amines (3 moles of the amine per mole of aqueous chromic acid) are processed to yield a product useful for the purposes of

this invention. The product, a clear brown viscous liquid, shows the following analyses:

Percent chromium	7.40
Percent nitrogen	6.11

Example 6

A product is prepared in the same manner set forth in Example 3, except that 596 grams of a commercial mixture of C_{18} – C_{24} tertiary-alkyl primary amines averaging about 20 carbon atoms per molecule is employed as the amine reactant.

Example 7

387 grams of CrO_3 is mixed with 244 grams of water to form a concentrated aqueous solution of chromic acid. Such solution is added to 1,000 grams of 2-ethylhexylamine (2 moles of amine per mole of aqueous chromic acid) over a period of 1.75 hours at 25°–96° C., the temperature rising as indicated due to the exothermic nature of the reaction. After all of the aqueous chromic acid has been added, the whole is stripped under a nitrogen atmosphere at 76° C./110 mm. Hg. to remove substantially all the water present. The product, a brown liquid, shows the following analyses:

Percent chromium	14.56
Percent nitrogen	6.23

COMPONENT B

This component, an acylated organic phosphate complex, is described in co-pending application, Serial No. 174,691, filed Feb. 21, 1962. It is prepared, as indicated earlier, by 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 5 moles of a copolymer of allyl alcohol and a styrene, (c) from about 0.5 to about 5 moles of an alkylphenol, and (d) from about 0.5 to about 4 moles of (b) employed of an unsaturated aliphatic carboxylic acid compound selected from the group consisting of high molecular weight unsaturated aliphatic carboxylic acid containing at least about 12 carbon atoms and esters of such acids; at a temperature within the range from about 50° C. to about 300° C. for about 0.5 to about 30 hours. In the interest of not unduly lengthening the present specification, it is intended that the disclosure of the above-identified co-pending application be considered as forming a part of the present specification.

Reagent (a) is, as indicated, selected from the group consisting of phosphorus pentoxide and phosphoric acid. For reasons of convenience, economy, and reactivity in preparing the acylated organic phosphate complex, phosphorus pentoxide is generally preferred. Where it is desired to employ phosphoric acids, 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 such 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) 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 5,000.

A particular preference is expressed for a copolymer of approximately equimolar amounts of allyl alcohol and styrene having an average molecular weight of about 1,100–1,150. 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, such as Monsanto RJ-100, which has an average molecular weight of about 1,580.

The term "a styrene" as used herein refers to styrene or any of the various substituted styrenes such as halogen-substituted styrenes, hydrocarbon-substituted styrenes, alkoxy-styrenes, acyloxy-styrenes, nitro-styrenes, etc. Examples of such substituted styrenes include para-chloro styrene, para-ethyl styrene, ortho-phenyl styrene, para-methoxy styrene, meta-nitro styrene, alpha-methyl styrene, 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) may be either a mono-alkyl or a poly-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 weight as high as 50,000 or more. Preferably the alkylphenol is a mono-alkylphenol in which the alkyl group contains from one to about 30 carbon atoms, preferably 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-isopropylphenol, para-tertiary butylphenol, ortho n-amyphenol, para-tertiary amyphenol, heptylphenol diisobutylphenol (i.e. isooctyl phenol), n-decylphenol, wax-alkylated alphanaphthol, 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, e.g., chloro, fluoro, nitro, alkoxy, sulfide, nitroso, etc. A particular preference is expressed for para-tertiary amyphenol. Also useful are polyhydric phenols such as alkylated resorcinol, alkylated catechols, alkylated pyrogallols, and their substitution products.

Reagent (d), the unsaturated aliphatic carboxylic acid compound, is a high molecular weight unsaturated aliphatic carboxylic acid containing at least 12 carbon atoms and/or an ester thereof. Illustrative of materials useful as this reagent are, for example, linoleic acid, linolenic acid, linseed oil, tung oil, tung oil acids, methyl linoleate, ethyl linolenate, chloroleic acid, phenyloleic acid, oleic acid, behenolic acid, palmitic acid, ricinoleic acid, ricinoleic acid, and mixtures of any of the foregoing.

Especially preferred are the unsaturated aliphatic carboxylic acids and/or esters thereof which contain at least 2 carbon-to-carbon double bonds such as linoleic acid, linseed oil, tung oil, and linolenic acid. A particular preference is expressed for linoleic acid and tung oil, both of which are readily available, staple articles of commerce. It is not necessary that the unsaturated acids and/or esters thereof be chemically pure materials. Crude linoleic acid obtained, for example, from the processing of tall oil has been found to be very suitable as Reagent (d) herein.

The process for the formation of the acylated organic phosphate complex may be carried out in any one of several different ways such as, for example; (1) preparing a mixture of Reagents (a, b, c, and d) and then heating such mixture at a temperature within the range from about 50° C. to about 300° C., preferably from about 80°-160° C., for about 0.5 to about 30 hours; (2) heating Reagent b, the copolymer of allyl alcohol and a styrene, with Reagent (d), the unsaturated aliphatic carboxylic acid compound, at a temperature within the range from about 50° C. to about 300° C., preferably 80°-200° C., to effect acylation of the copolymer and then adding Reagents a and c and continuing the heating, the total reaction time being from about 0.5 to about 30 hours; and (3) heating Reagents (a,b, and c) at a temperature within the range from about 50° C. to about 300° C., preferably 75-150° C., and then effecting the acylation of such intermediate product with Reagent (d), the unsaturated ali-

phatic carboxylic acid compound, at temperatures within the range from about 50° C. to about 300° C., preferably 80°-200° C., the total reaction time being from about 0.5 to about 30 hours.

Generally it is most convenient to prepare the acylated organic phosphate complex in the presence of an inert, volatile solvent which serves to reduce the viscosity of the reaction mass. The solvent may remain, if desired, in the final product. Any of the solvents ordinarily employed in the paint and varnish industry may be used for this purpose such as, e.g., benzene, xylene, toluene, mesitylene, cyclohexane, methylcyclohexane, aromatic petroleum spirits, chlorobenzene, trichloroethylene, tetrachloroethylene, ethylene dichloride, dioxane, turpentine, diisopropyl ether, and the like. Mixtures of two or more of the foregoing solvents may also be used. In some instances, however, it is preferred to conduct the process in the absence of solvent and then, optionally, to dilute the acylated organic phosphate complex with the desired solvent or mixture of solvents.

The precise chemical composition of the acylated organic phosphate complex employed as Component B herein is not known. It is believed, however, that the phosphorus-containing reagent and the unsaturated aliphatic carboxylic acid compound phosphorylate and acylate the organic hydroxy compounds present to form, respectively, acid phosphate ester groups and carboxylic acid ester groups. Other reactions such as polymerization and/or etherification may also occur during the process and it is not intended that the theories and evidence presented herein be interpreted in any manner which would limit the scope of the invention except as as the latter is defined by appended claims.

The following examples are presented to illustrate specific modes of preparing Component B. All parts are by weight unless otherwise specified. The "strong acid number" is reported for the solvent-free acylated organic phosphate complex and is determined using bromphenol blue as the end point indicator. Such strong acid number denotes the number of milligrams of potassium hydroxide required to neutralize one gram of solvent-free product in the presence of an indicator such as bromphenol blue which changes color in the region of pH 4. Acid-base neutralizations or titrations conducted in this manner measure acidity due to acid phosphates but do not measure acidity due to carboxylic acid.

Example 8

210 parts (0.75 mole) of linoleic acid, 288 parts (0.25 mole) of Polyol X-450, 283 parts of xylene solvent, and 4 parts of para toluenesulfonic acid catalyst are introduced into a reaction vessel and stirred thoroughly. The whole is then heated to about 143° C. and maintained at this temperature for 4 hours while water of esterification is removed by means of a side-arm water trap. The crude acylated Polyol X-450 thus obtained is washed with 500 parts of water to remove the esterification catalyst and then it is dried by azeotropic distillation, returning the xylene by means of a side-arm water trap.

949 parts (0.24 mole) of the acylated Polyol X-450, 79 parts (0.48 mole) of para-tertiary amyphenol, 36 parts (0.25 mole) of phosphorus pentoxide, and 115 parts of xylene solvent are reacted at the reflux temperature (ca. 143° C.) for 6 hours.

The resulting 50 percent solution in xylene of the desired acylated organic phosphate complex shows the following analyses.

Percent phosphorus	1.28
Strong acid number	49

Example 9

575 parts (0.5 mole) of Polyol X-450, 468 parts (0.5 mole) of boiled linseed oil, 164 parts (1.0 mole) of para-tertiary amyphenol, 71 parts (0.5 mole) of phosphorus pentoxide, and 1,278 parts of xylene are placed in a flask

and stirred vigorously. The whole is refluxed for 6 hours while water is removed by means of a side-arm water trap. The product, a 50 percent solution of the desired acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus -----	1.15
Strong acid number -----	42

Example 10

460 parts (0.4 mole) of Polyol X-450 is acylated with 336 parts (1.2 moles) of linoleic acid in 775 parts of xylene solvent over a period of 10 hours at the reflux temperature.

1,451 parts (0.38 mole) of the above acylated Polyol X-450, 125 parts (0.76 mole) of para-tertiary amylphenol, 54 parts (0.38 mole) of phosphorus pentoxide, and 179 parts of xylene solvent are heated for 8 hours at the reflux temperature. The product, a 50 percent solution of the acylated organic phosphate complex in xylene solvent, shows the following analyses.

Percent phosphorus -----	1.33
Strong acid number -----	52

Example 11

575 parts (0.5 mole) of Polyol X-450, 598 parts (2.0 moles) of methyl linoleate, 164 parts (1.0 mole) of para-tertiary amylphenol, 71 parts (0.5 mole) of phosphorus pentoxide, and 1,408 parts of xylene solvent are introduced into a reaction vessel and stirred vigorously. The whole is then heated for 6 hours at the reflux temperature while water is removed by means of a side-arm water trap. The product, a 50 percent solution of the acylated organic phosphate complex in xylene solvent, shows the following analyses.

Percent phosphorus -----	0.99
Strong acid number -----	36

Example 12

575 parts (0.5 mole) of Polyol X-450, 431 parts (1.5 mole) of methyl linoleate, 164 parts (1.0 mole) of para-tertiary amylphenol, 71 parts (0.5 mole) of phosphorus pentoxide, and 1,241 parts of xylene solvent are introduced into a reaction vessel and stirred vigorously. The whole is then heated for 6 hours at the reflux temperature and the water of reaction is removed by means of a side-arm water trap. The product, a 50 percent solution of the acylated organic phosphate complex in xylene solvent, shows the following analyses.

Percent phosphorus -----	1.26
Strong acid number -----	54

Example 13

575 parts (0.5 mole) of Polyol X-450 is acylated with 140 parts (0.5 mole) of linoleic acid and 112 parts (0.5 mole) of tung oil acids in 800 parts of xylene solvent over a period of 8 hours at the reflux temperature. The water of esterification evolved is removed by means of a side-arm water trap.

1,500 parts (0.75 mole) of the above acylated Polyol X-450, 249 parts (1.52 moles) of para-tertiary amylphenol, 107 parts (0.75 mole) of phosphorus pentoxide and 356 parts of xylene are introduced into a reaction vessel and stirred vigorously. The whole is then heated for 6 hours at the reflux temperature. The resulting product, a 50 percent solution of the acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus -----	2.19
Strong acid number -----	76

Example 14

575 parts (0.5 mole) of Polyol X-450 is acylated with 420 parts (1.5 moles) of linoleic acid in 968 parts of xylene solvent containing 0.5 part of para toluenesul-

fonic acid as an esterification catalyst. The acylation is effected by heating the whole for a period of 12 hours at the reflux temperature while the water of esterification is removed by means of a side-arm water trap.

1271 parts (0.33 mole) of the above acylated Polyol X-450, 492 parts (3.0 moles) of para-tertiary amylphenol, 142 parts (1.0 mole) of phosphorus pentoxide, and 633 parts of xylene solvent are introduced into a reaction vessel and stirred vigorously. The whole is then heated at the reflux temperature for 6 hours to yield the product, a 50 percent solution of an acylated organic phosphate complex in xylene. It shows the following analyses.

Percent phosphorus -----	2.25
Strong acid number -----	90

Example 15

522 parts (0.4 mole) of an acylated Polyol X-450 prepared in the manner set forth in Example 14, 392 parts (2.4 moles) of para-tertiary amylphenol, 114 parts (0.8 mole) of phosphorus pentoxide, and 506 parts of xylene solvent are stirred together for 6 hours at about 143° C. The product, a 50 percent solution of the acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus -----	3.01
Strong acid number -----	112

Example 16

1,042 parts (0.8 mole) of an acylated Polyol X-450 prepared in the manner set forth in Example 14, 197 parts (1.2 moles) of para-tertiary amylphenol, 57 parts (0.4 mole) of phosphorous pentoxide, and 254 parts of xylene are introduced into a reaction vessel and stirred vigorously. The whole is heated for 5 hours at the reflux temperature while water is removed by means of a side-arm water trap. The product, a 50 percent solution of the acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus -----	1.50
Strong acid number -----	66

Example 17

750 parts (0.5 mole) of Polyol X-450 is acylated with 112 parts (0.5 mole) of tung oil acids in xylene solution (853 parts of xylene) over a period of 6 hours at the reflux temperature. The water of esterification is removed by means of a side-arm water trap.

1,355 parts (0.5 mole) of this acylated Polyol X-450, 246 parts (1.5 mole) of para-tertiary amylphenol, 71 parts (0.5 mole) of phosphorus pentoxide, and 317 parts of xylene solvent are introduced into a flask and stirred vigorously. The whole is stirred for 6 hours at the reflux temperature while water is removed by means of a side-arm water trap. The product, a 50 percent solution of the acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus -----	1.58
Strong acid number -----	58

Example 18

460 parts (0.4 mole) of Polyol X-450 is acylated with 336 parts (1.2 mole) of linolenic acid in xylene solution over a period of 6 hours at the reflux temperature. The water of esterification is removed by means of a side-arm water trap.

1,451 parts (0.38 mole) of the above acylated Polyol X-450, 125 parts (0.76 mole) of para-tertiary amylphenol, 54 parts (0.38 mole) of phosphorus pentoxide, and 179 parts of xylene solvent are introduced into a flask and stirred vigorously. The whole is then refluxed for 6 hours while water is removed by means of a side-arm water trap. The product, a 50 percent solution of

11

the acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus	1.31
Strong acid number	56

Example 19

575 parts (0.50 mole) of Polyol X-450 is acylated with 287 parts (1.0 mole) of tung oil acids in xylene solvent (844 parts) over a period of 8 hours at the reflux temperature. The water of esterification is removed by means of a side-arm water trap.

1,300 parts (0.39 mole) of this acylated Polyol X-450, 191 parts (1.16 mole) of para-tertiary amylphenol, 55 parts (0.39 mole) of phosphorus pentoxide, and 246 parts of xylene solvent are introduced into a flask and stirred vigorously. The whole is then refluxed for 4 hours. The product, a 50 percent solution of the acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus	1.38
Strong acid number	46

Example 20

575 parts (0.5 mole) of Polyol X-450 is acylated with 141 parts (0.5 mole) of oleic acid in 707 parts of xylene solvent over a period of 8 hours at 140° C. The water of esterification is removed by means of a side-arm water trap.

1,364 parts (0.48 mole) of this acylated Polyol X-450, 237 parts (1.45 mole) of para-tertiary amylphenol, 68 parts (0.48 mole) of phosphorus pentoxide, and 305 parts of xylene solvent are introduced into a flask and stirred vigorously. The whole is then heated 8 hours at the reflux temperature while the water of reaction is removed by means of a side-arm water trap. The product, a 50 percent solution of the acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus	1.53
Strong acid number	54

Example 21

575 parts (0.5 mole) of Polyol X-450 is acylated with 140 parts (0.5 mole) of linoleic acid in 707 parts of xylene solvent containing 5 parts of para toluenesulfonic acid catalyst over a period of 4 hours at the reflux temperature. The water of esterification is removed by means of a side-arm water trap and the reaction mixture is washed with warm water to remove the small amount of sulfonic acid catalyst employed.

530 parts (0.32 mole) of this acylated Polyol X-450, 52 parts (0.32 mole) of para-tertiary amylphenol, 23 parts (0.16 mole) of phosphorus pentoxide, and 75 parts of xylene are introduced into a flask and stirred vigorously. The whole is then heated at the reflux temperature for about 6 hours. The product, a 50 percent solution of the acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus	1.37
Strong acid number	46

Example 22

1,150 parts (1.0 mole) of Polyol X-450, 852 parts (3.0 moles) of crude linoleic acid derived from tall oil, 2,400 parts of xylene solvent, 328 parts (2.0 moles) of para-tertiary amylphenol, and 142 parts (1.0 mole) of phosphorous pentoxide are introduced into a reaction flask fitted with a side-arm water trap. The whole is heated for 4.5 hours at the reflux temperature to yield the product, at 50 percent solution of the acylated organic phosphate complex in xylene. It shows the following analyses.

Percent phosphorus	1.14
Strong acid number	62

12

Example 23

1,150 parts (1.0 mole) of Polyol X-450, 852 parts (3.0 moles) of linoleic acid, 1,209 parts of xylene solvent, 328 parts (2.0 moles) of para-tertiary amylphenol, and 230 parts (2.0 moles) of commercial, 85 percent orthophosphoric acid are introduced into a flask equipped with a side-arm water trap. The whole is stirred and heated at the reflux temperature for 6.5 hours to yield the product, a 66.6 percent solution of the acylated organic phosphate complex in xylene. It shows the following analyses.

Percent phosphorus	1.21
Strong acid number	45

Example 24

2,155 parts (1.875 moles) of Polyol X-450, 710 parts (2.5 moles) of crude linoleic acid derived from tall oil, 2,310 parts of xylene solvent, 1,155 parts (7.05 moles) of para-tertiary amylphenol, and 355 parts (2.5 moles) of phosphorus pentoxide are introduced into a reaction vessel equipped with a stirrer and a side-arm water trap. The whole is heated for 2 hours at the reflux temperature to yield the product, a 65 percent solution of the acylated organic phosphate complex in xylene, which shows the following analyses.

Percent phosphorus	2.47
Strong acid number	60

Example 25

719 parts (0.625 mole) of Polyol X-450, 164 parts (1.0 mole) of para-tertiary amylphenol, and 71 parts (0.5 mole) of phosphorus pentoxide, and 952 parts of xylene solvent are introduced into a flask fitted with a stirrer and a side-arm water trap. The whole is refluxed for 6 hours while the water of reaction is removed as formed.

494 parts (0.641 mole) of the resulting organic phosphate complex is acylated with 179 parts (0.641 mole) of linoleic acid over a 7 hour period at 154° C. The water of esterification is removed as formed by means of a side-arm water trap. The product, a 63 percent solution of the acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus	1.02
Strong acid number	32

Example 26

383 parts (0.33 mole) of Polyol X-450, 284 parts (1.0 mole) of linoleic acid, and 5 ml. of commercial, 85 percent phosphoric acid are heated for 3 hours at 140-147° C. while the water of esterification is permitted to escape from the reaction vessel. Thereafter, 109 parts (0.66 mole) of para-tertiary amylphenol and 77 parts (0.66 mole) of commercial, 85 percent phosphoric acid are added and the whole is heated for an additional 14.5 hours at 143-150° C., while the water of reaction is removed as formed by means of a side-arm water trap. The solvent-free, acylated organic phosphate complex is diluted with 254 parts of aromatic petroleum spirits to lessen its viscosity. The product shows the following analyses.

Percent phosphorus	2.11
Strong acid number	69

Example 27

863 parts (0.75 mole) of Polyol X-450 is acylated with 639 parts (2.25 moles) of linoleic acid in 1,461 parts of xylene solvent over a period of 7.5 hours at 142-144° C. The water of esterification is removed as formed by means of a side-arm water trap. Thereafter, 246 parts (1.5 moles) of para-tertiary amylphenol, 388 parts of xylene solvent, and 142 parts (1.0 mole) of phosphorus pentoxide are added and the whole is heated for an additional 6 hours at 143° C. The water of reaction is removed by means of the side-arm water trap. The prod-

uct, a 50 percent solution of the acylated organic phosphate complex in xylene, shows the following analyses.

Percent phosphorus ----- 1.42
Strong acid number ----- 72

The compositions of this invention may be applied to metal articles 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 corrosion-proofing composition or of a coating composition containing the same 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 dried film thickness of the corrosion-proofing composition of this invention or of a 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 article. 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 corrosion-proofing composition of this invention 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.

As indicated earlier, the corrosion-proofing compositions of this invention comprise from about 0.05 to about 20 parts by weight of Component A per part of Component B. When Components A and B are mixed there is a slight, but perceptible, rise in temperature. Analytical evidence indicates that upon mixing, at least a portion of the hexavalent chromium in Component A is reduced to trivalent chromium. In any event, Components A and B may be pre-mixed and packaged, mixed just prior to use, or blended with a known siccative organic composition prior to packaging or just prior to application to a metal article.

A number of laboratory tests were carried out to determine the utility of the hereindescribed corrosion-proofing compositions as protective coating compositions per se for metal articles, as primers to prepare a metal article to receive a top-coat of a siccative organic coating composition, and as improving agents for use in known siccative organic coating compositions. Unless otherwise indicated, all parts and percentages are by weight.

Example A

Two 4-inch x 8-inch panels of 20-gauge SAE 1020 cold-rolled steel were spray-coated, respectively, with an acylated organic phosphate primer and with a corrosion-proofing composition of this invention. The acylated organic phosphate primer consisted of a blend of 800 parts of the product of Example 8 and 200 parts of isobutanol solvent. The corrosion-proofing composition of this invention consisted of a blend of 720 parts of the product of Example 8, 20 parts each of the products of Examples 3 and 4, and 240 parts of isobutanol solvent. The dried film thickness on each panel (air-dried for 4 days) was found to be 0.5 ± 0.1 mil.

Thereafter, each panel was spray-coated with a flat, air-dry, high-solids content commercial alkyd white paint. When the top-coat had dried, it was inspected for the incidence of crazing (i.e., development of minute, hair-line cracks). The panel which had received a priming coat of the acylated organic phosphate primer was heavily crazed. On the other hand, the panel which had received a priming coat of the corrosion-proofing composition of this invention showed no crazing whatever.

Example B

An experiment like that described in Example A was carried out, except that the steel panels, before priming and top-coating, were pre-rusted by outdoor exposure for two months.

The pre-rusted panel which had received a priming coat of the acylated organic phosphate primer was heavily crazed, whereas the pre-rusted panel which had received a priming coat of the corrosion-proofing composition of this invention showed no crazing whatever.

Example C

Two 4-inch x 8-inch panels of hot-dip galvanized 20-gauge SAE 1020 cold-rolled steel were brush-coated, respectively, with two different corrosion-proofing compositions of this invention. A third and similar panel received no priming coat (for purposes of control).

Thereafter, each panel was brush-coated with a glossy, air-dry, commercial alkyd white paint and allowed to air-dry for 7 days. The painted panels were then subjected to the Salt Fog Corrosion test described in ASTM procedure B117-57T. In this test a mist or fog of 5 percent aqueous sodium chloride is maintained in contact with the panels for a predetermined time (in this case, 120 hours) at $95^\circ \pm 2^\circ$ F. The panels were removed from the Salt Fog chamber, washed with tap water to remove any salt deposits, and scraped vigorously with a putty knife to dislodge any loosened paint. The scraped panels were inspected to determine the percent of paint still adhered to the galvanized metal substrate. The results of the inspection are given in Table I.

TABLE I

Salt fog corrosion test, 120 hours

Priming composition applied to the galvanized steel panel:

	Percent of paint adhered after test
(1) A blend of 180 parts of the product of Example 8, 11 parts of the product of Example 1, and 59 parts of isobutanol solvent -----	85
(2) A blend of 180 parts of the product of Example 8, 11 parts of the product of Example 2, and 59 parts of isobutanol solvent -----	95
(3) No priming composition (control) -----	0

It will be noted that each of two different priming compositions of this invention markedly improved the adhesion of a commercial paint to a galvanized ferrous metal substrate in a corrosive atmosphere.

Example D

Three panels were prepared in the same manner set forth in Example C and subjected to a high humidity test. In this test, the panels were placed in a chamber wherein an atmosphere of 100 percent humidity at 100° F. is maintained. After five weeks in the chamber, the panels were removed and scraped with a spatula to determine the degree of adhesion of the paint to the galvanized metal substrate. The test results are shown in Table II.

TABLE II

100 percent humidity exposure test, 5 weeks

Priming composition applied to the galvanized steel panel:

	Inspector's remarks
(1) Composition (1) of Table I -----	Good adhesion; very difficult to remove any paint.
(2) Composition (2) of Table I -----	Do.
(3) No priming composition (control) -----	Very poor adhesion; the paint film was completely removed upon scraping. Some corrosion of the metal substrate was evident.

15

The above results clearly indicate that compositions of this invention, when employed as primers on galvanized ferrous metal articles, substantially improve the adhesion thereto of a subsequently applied siccative organic coating composition under conditions of high humidity.

Example E

A 4-inch x 8-inch panel of 20-gauge SAE 1020 cold-rolled steel was brush-coated with a clear film alkyd resin primer consisting of a blend of 80 parts of a commercial alkyd resin, 20 parts of xylene, 1 part of a solution of cobalt naphthenate in aromatic petroleum spirits having a cobalt content of 1 percent, 1 part of a solution of lead naphthenate in aromatic petroleum spirits having a lead content of 4 percent, and 1.5 parts of a proprietary anti-skinning agent.

A similar panel was brush-coated with a clear film primer of this invention consisting of a blend of 4.5 parts of the product of Example 2, 72 parts of the product of Example 8, and 23.5 parts of aromatic petroleum spirits.

The primed panels, labeled Panel Y and Panel Z, respectively, were subjected to the Salt Fog Corrosion test described in Example C, modified only in that the test duration was 48 hours and that the exposed panels were water-washed (not scraped) to remove any non-adherent film. The test results are shown in Table III.

TABLE III

Salt fog corrosion test, 48 hours

Primed steel panel:	Percent of primer adhered
Y (control; known primer) -----	15 (exposed metal substrate badly rusted).
Z (primer of this invention) -----	96 (no rust on metal substrate).

It will be noted that a primer of this invention adhered far better than a known commercial to a ferrous metal article. It also showed superior rust-proofing properties.

Example F

A 4-inch x 8-inch panel of 20-gauge SAE 1020 cold-rolled steel was brush-coated with a primer made according to Federal specification TTP-00615b from 4,590 parts of basic lead silicochromate, 22.5 parts of castor wax, 270 parts of pigment grade Fe_2O_3 , 1560 parts of linseed oil, 620 parts of a commercial alkyd resin, 655 parts of mineral spirits, and 11.25 parts each of a solution of cobalt naphthenate in mineral spirits having a cobalt content of 6 percent and a solution of lead naphthenate in mineral spirits having a lead content of 24 percent.

A similar steel panel was brush-coated with a primer like that described above except that 140 parts of the alkyd resin and 60 parts of the mineral spirits were replaced with 200 parts of a corrosion-proofing composition of this invention consisting of 14 percent of the product of Example 2, 75 percent of the product of Example 8, and 11 percent of aromatic petroleum spirits.

The primed panels labeled Panel V and Panel W, respectively, were then subjected to the Salt Fog Corrosion test described in Example C, but modified in the following respects:

(1) Test duration was 288 hours.

(2) Each primed panel, before insertion in the Salt Fog chamber, was scribed with a sharp steel instrument to yield a deep score beginning one inch from the top of the panel and ending one inch from the bottom thereof.

(3) The exposed panels were water-washed (not scraped) to remove any non-adherent film.

The test results are recorded in Table IV.

16

TABLE IV

Salt fog corrosion test, 288 hours

Primed steel panel:	Percent of primer adhered
V (control primer) -----	65
W (control primer blended with a corrosion-proofing composition of this invention) -----	80

It will be noted that a corrosion-proofing composition of this invention, when used as an improving agent in a known primer, substantially improved the adhesion thereof to a ferrous metal article.

Example G

A 4-inch x 8-inch panel of pre-rusted 20-gauge SAE 1020 cold-rolled steel like that described in Example B was brush-coated with a primer made according to Federal specification TTP-86bI from 6200 parts of red lead, 16 parts of aluminum stearate, 872 parts of raw linseed oil, 304 parts of bodied linseed oil, 560 parts of mineral spirits, and 48 parts of a solution of cobalt naphthenate in mineral spirits having a cobalt content of 1 percent.

A similar pre-rusted panel was brush-coated with a primer similar to the above, except that 120 parts each of the raw linseed oil and mineral spirits were replaced with 240 parts of a corrosion-proofing composition of this invention consisting of 90 parts of the product of Example 7, 60 parts of the product of Example 8, and 90 parts of mineral spirits.

The primed panels, labeled T and U, respectively, were then subjected to the Salt Fog Corrosion test described in Example C, but modified in the following respects:

(1) Each primed panel, before insertion in the Salt Fog chamber, was scribed with a sharp steel instrument to yield a deep score beginning one inch from the top of the panel and ending one inch from the bottom thereof.

(2) The exposed panels were water-washed to remove any non-adherent film.

The test results are recorded in Table V.

TABLE V

Salt fog corrosion test, 120 hours

Primed, pre-rusted steel panel:	Percent of primer adhered
T (control primer) -----	5
U (control primer containing a corrosion-proofing composition of this invention) -----	90

It will be noted that once again a composition of this invention markedly improved the adhesion of a known primer to a ferrous article.

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

What is claimed is:

1. A liquid corrosion-proofing composition adapted to form a protective coating on metal articles which comprises the combination of:

(A) from about 0.05 to about 20 parts by weight of the product obtained by mixing one mole of at least one aliphatic amine containing from about 6 to 30 carbon atoms with from about 0.25 to about 2 moles of aqueous chromic acid and heating the mixture to remove substantially all water present, and

(B) 1 part by weight of an acylated 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 5 moles of a copolymer of allyl alcohol and a styrene,

(c) from about 0.5 to about 5 moles of an alkylphenol, and

(d) from about 0.5 to about 4 moles per mole of

(b) employed of an unsaturated aliphatic monocarboxylic acid compound selected from the group consisting of high molecular weight unsaturated aliphatic monocarboxylic acids containing at least about 12 carbon atoms and esters of such acids,

at a temperature within the range from about 50° C. to about 300° C. for about 0.5 to about 30 hours.

2. A corrosion-proofing composition in accordance with claim 1 further characterized in that the aliphatic amine reactant of (A) is a monoalkyl primary amine.

3. A corrosion-proofing composition in accordance with claim 1 further characterized in that the aliphatic amine reactant of (A) is a mixture of C₁₂ to C₁₅ tertiary-alkyl primary amines.

4. A corrosion-proofing composition in accordance with claim 1 further characterized in that the aliphatic amine reactant of (A) is 2-ethyl-hexylamine.

5. A corrosion-proofing composition in accordance with claim 1 further characterized in that the phosphorus-containing reagent of (B) is phosphorus pentoxide.

6. A corrosion-proofing composition in accordance with claim 1 further characterized 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 of 1,100 to 1,150.

7. A corrosion-proofing composition in accordance with claim 1 further characterized in that the alkylphenol of (B) is para-tertiary amylphenol.

8. A corrosion-proofing composition in accordance with claim 1 further characterized in that the unsaturated aliphatic monocarboxylic acid compound of (B) is linoleic acid.

9. A method for inhibiting the corrosion of a metal article which comprises applying thereto a film comprising the composition of claim 1.

10. A metal article which has been protected against corrosion in accordance with the method of claim 9.

11. A method for inhibiting the corrosion of a metal article which comprises applying thereto a film comprising a major proportion of a siccative organic coating composition selected from the group consisting of paints, varnishes, lacquers, primers, synthetic resins and enamels and a minor proportion of the composition of claim 1.

12. A method for inhibiting the corrosion of a metal article which consists of first applying thereto a film of the composition of claim 1 and subsequently applying thereto a film of a siccative organic coating composition selected from the group consisting of paints, varnishes, lacquers, primers, synthetic resins and enamels.

13. A metal article which has been protected against corrosion in accordance with the method of claim 11.

14. A metal article which has been protected against corrosion in accordance with the method of claim 12.

References Cited by the Examiner

UNITED STATES PATENTS

2,270,386	1/1942	Sloan	260—438
3,055,865	9/1962	Craig	260—33.2

FOREIGN PATENTS

757,043	9/1956	Great Britain.
---------	--------	----------------

ALEXANDER H. BRODMERKEL, *Primary Examiner.*

MORRIS LIEBMAN, ALFRED L. LEAVITT,
Examiners.