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3,276,916 INHIBITION OF CORROSION OF METAL SURFACES

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15 Claims. (Cl. 148—6.16)

This application is a division of application Ser. No. 139,845, filed September 22, 1961, and now U.S. Patent No. 3,215,715.

The present invention relates to novel, metal-containing organic phosphate complexes and to a process for their preparation.

In a more specific sense, it relates to the inhibition of corrosion of metal surfaces by means of such metal complexes.

The corrosion of metal surfaces 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 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 either or both moisture and oxygen from contact with the ferrous metal surface. Such coatings are, of course, subject to abrasion and other forms of physical deformation and to the extent that these coatings are penetrated or otherwise destroyed by such influences they become ineffective for the desired purpose. It is important that such coatings provide complete protection of all of the ferrous metal surface. If there is any portion of such a surface which is not so protected, regardless of how small the unprotected surface may be, the degree of protection afforded is considerably less than needed. A satisfactory corrosion-inhibiting coating, then, must have the ability to resist substantial deformation upon impact, abrasion, etc., so that a uniform and complete film is maintained in the face of such adverse influences.

Metal salts of acid esters of phosphoric or phosphorothioic acids have been investigated by workers engaged in the task of providing protective coatings for metal. 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 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 various complex phosphorothioic acids are effective in preventing or retarding the corrosion of metals.

Although such salt-esters of phosphoric and phosphorothioic acids have provided means for combatting 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 under certain conditions. 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.

It is accordingly an object of the present invention to provide novel metal-containing organic phosphate complexes and a process for their preparation.

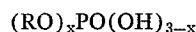
Another object is to provide a means for protecting metal surfaces from the ravages of corrosion.

A still further object is to provide a means for substantially increasing the corrosion resistance of phosphated metal surfaces.

These and other objects of the invention are realized by means of a process for preparing a metal containing organic phosphate complex which comprises the reaction of (A) a polyvalent metal salt of the acid phosphate esters derived from the reaction of phosphorus pentoxide with a mixture of a monohydric alcohol and from 0.25 to 4.0 equivalents of a polyhydric alcohol, with (B) at least about 0.1 equivalent of an organic epoxide.

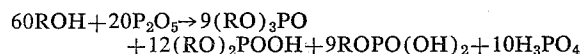
Thin films of the aforesaid complexes are effective in inhibiting the corrosion of metal surfaces, especially phosphated ferrous metal surfaces.

The acid phosphate esters required for the preparation of starting material (A) are made, as indicated, by the reaction of phosphorus pentoxide with a mixture of a monohydric alcohol and a polyhydric alcohol. The precise nature of this reaction is not entirely clear, but it is known that a mixture of phosphate esters is formed. This mixture consists principally of acid phosphate esters, i.e., compounds of the general formula:



where x equals 1 or 2 and R is an organic radical, although some neutral tri-esters of the formula $(RO)_3PO$ may also be formed.

Likewise, the stoichiometry of the reaction is not clear. Based on theoretical consideration alone, it appears that the following products are formed:



In actual practice, the reaction does not take place in the quantitative fashion indicated by the above equation. A complex mixture of different esters results, the relative proportions of which can be altered by varying the amount of alcohol used from 2 to 6 equivalents per mole of P_2O_5 .

The nature and the stoichiometry of the reaction are complicated further in the present invention by the fact that one of the reactants is a polyhydric alcohol. Theoretical considerations indicate that a polyhydric alcohol forms cyclic and/or polymeric phosphate esters when it reacts with phosphorus pentoxide. Indeed, the tenacious character of the film formed on metal surfaces by the complexes of this invention is believed to be due at least in part to the presence of such cyclic and/or polymeric structures.

In any event, the acid phosphate esters resulting from the reaction of one mole of phosphorus pentoxide with from about 2 to about 6 equivalents of a mixture of monohydric and polyhydric alcohols are useful in the preparation of starting material (A). The term "equivalent" as used herein reflects the hydroxyl equivalency of the alcohol. Thus, for example, 1 mole of octyl alcohol is 1 equivalent thereof, 1 mole of ethylene glycol is 2 equivalents thereof, 1 mole of glycerol is 3 equivalents thereof, etc.

Less than 2 or more than 6 equivalents of alcohol can be used, if desired, in the reaction with one mole of phosphorus pentoxide, although such amounts are not preferred for reasons of economy. When fewer than 2 equivalents of alcohol are used, some unreacted phosphorus pentoxide may remain in the product or precipitate therefrom. On the other hand, when substantially more than 6 equivalents of alcohol are used, unreacted alcohol would be present in the product. For the purpose of the present invention it is generally preferred to employ from about 3 to about 5 equivalents of the alcohol mixture per mole of phosphorus pentoxide.

The monohydric alcohols useful in the preparation of starting material (A) are principally the non-benzenoid alcohols, i.e., the aliphatic and cycloaliphatic alcohols, although in some instances aromatic and/or heterocyclic substituents may be present. Thus, suitable monohydric alcohols are, e.g., propyl, isopropyl, butyl, isobutyl, amyl, hexyl, cyclohexyl, heptyl, methyl-cyclohexyl, octyl, isooctyl, decyl, lauryl, tridecyl, oleyl, benzyl, betaphenethyl, alpha-pyridylethyl, etc., alcohols. Mixtures of such alcohols can also be used if desired. Substituents such as, e.g., chloro, bromo, fluoro, nitro, nitroso, ester, ether, sulfide, keto, etc., which do not prevent the desired reaction may also be present in the alcohol. In most instances, however, the monohydric alcohol will be an unsubstituted alkanol.

The polyhydric alcohols useful in the preparation of starting material (A) are principally glycols, i.e., dihydric alcohols, although trihydric, tetrahydric, and higher polyhydric alcohols may also be used. In certain instances, they may contain aromatic and/or heterocyclic substituents as well as chloro, bromo, fluoro, nitro, nitroso, ether, ester, sulfide, keto, etc., substituents. Thus, suitable polyhydric alcohols are, e.g., ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, 1,3-butanediol, glycerol, glycerol monooleate, mono-phenyl ether of glycerol, mono-benzyl ether of glycerol, 1,3,5-hexanetriol, pentaerythritol, sorbitol dioctanoate, pentaerythritol dioleate, and the like. In lieu of a single polyhydric alcohol, mixtures of two or more of such alcohols may be employed.

As indicated, starting material (A) is prepared from a mixture of monohydric and polyhydric alcohols. The mixture may contain a single monohydric and a single polyhydric alcohol, or a plurality of one of both of such alcohols. For the purpose of this invention, best results are achieved when there is present from 0.25 to about 4.0 equivalents of polyhydric alcohol per equivalent of monohydric alcohol. The use of mixtures outside of this range tends to produce either intractable esters, or esters which, when converted to the complex of this invention, are deficient in film forming properties. Mixtures of iso-octyl alcohol and dipropylene glycol are very satisfactory and a particular preference is expressed for a mixture in which these alcohols, respectively, are present in about equivalent amounts.

The reaction between the alcohol mixture and phosphorus pentoxide is exothermic and can be carried out conveniently at a temperature ranging from room temperature or below to a temperature just beneath the decomposition point of the mixture. Generally, reaction temperatures within the range of from about 40° C. to about 200° C. are most satisfactory. The reaction time required varies according to the temperature and to the hydroxyl activity of the alcohols. At the higher temperatures, as little as 5 or 10 minutes may be sufficient for complete reaction. On the other hand, at room temperature 12 or more hours may be required. Generally it is most convenient to heat the alcohol mixture with phosphorus pentoxide for 0.5 to 8 hours at 60–120° C. In any event, the reaction is carried out until periodic acid number determinations on the reaction mass indicate that no more acid phosphate esters are being formed.

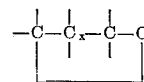
To facilitate mixing and handling, the reaction may be conducted in the presence of an inert solvent. Generally such solvent is a petroleum distillate hydrocarbon, an aromatic hydrocarbon, an ether, or a lower chlorinated alkane, although mixtures of any such solvents can be used. Typical solvents include, e.g., petroleum aromatic spirits boiling in the range 250°–400° F., benzene, xylene, toluene, mesitylene, ethylene dichloride, diisopropyl ether, etc. In most instances, the solvent is allowed to remain in the acid phosphate esters and ultimately the final metal-containing organic phosphate complex, where it serves as a vehicle for the convenient application of films of the complex to metal surfaces.

The conversion of the acid phosphate esters to the polyvalent metal salt may be carried out by any of the various known methods for the preparation of salts of organic acids such as, e.g., reaction of the acid-esters with a polyvalent metal base such as a metal oxide, hydroxide, or carbonate. Other suitable methods include, e.g., reaction of the acid-esters with a finely divided polyvalent metal, or the metathesis of a monovalent metal salt of the acid-esters with a soluble salt of the polyvalent metal such as e.g., a nitrate, chloride, or acetate thereof.

The polyvalent metal of starting material (A) may be any light or heavy polyvalent metal such as, e.g., zinc, cadmium, lead, iron, cobalt, nickel, barium, calcium, strontium, magnesium, copper, bismuth, tin, chromium or manganese. A preference is expressed for the polyvalent metals of Group II of the Periodic Table and of these, zinc is particularly preferred. A highly effective starting material (A) for the purpose of the present invention is the zinc salt of the acid phosphate esters formed by the reaction of a mixture of equivalent amounts of isooctyl alcohol and dipropylene glycol with phosphorus pentoxide.

The formation of the metal-containing organic phosphate complex of this invention involves, as indicated, a reaction between starting material (A), the polyvalent metal salt of certain acid phosphate esters, and starting material (B), the organic epoxide.

The organic epoxides, i.e., compounds containing at least one



linkage where x is zero or a small integer, suitable for the purpose of this invention include the various substituted and unsubstituted alkylene oxides containing at least two aliphatic carbon atoms, such as, e.g., ethylene oxide, 1,2-propylene oxide, 1,3-propylene oxide, 1,2-butylene oxide, pentamethylene oxide, hexamethylene oxide, 1,2-octylene oxide, cyclohexene oxide, methyl cyclohexene oxide, 1,2; 11,12-diepoxydodecane, styrene oxide, alpha-methyl styrene oxide, beta-propiolactone, methyl epoxycaprylate, ethyl epoxypalmitate, propyl epoxymyristate, butyl epoxystearate, epoxidized soyabean oil, and the like. Of the various available organic epoxides, it is preferred to use those which contain at least 12 carbon atoms. Especially preferred are those epoxides, which contain at least 12 carbon atoms and also a carboxylic ester group in the molecule. Thus, the commercially available epoxidized carboxylic ester, butyl epoxystearate is very satisfactory as starting material (B) for the purpose of this invention. If desired, the organic epoxide may also contain substituents such as, e.g., chloro, bromo, fluoro, nitro, nitroso, ether, sulfide, keto, etc., in the molecule.

The stoichiometry of the reaction of the polyvalent metal salt of the acid phosphate esters, starting material (A), with the organic epoxide, starting material (B), to form the metal-containing organic phosphate complex of this invention is not precisely known. There are indications, however, that the reaction involves about one equivalent each of the polyvalent metal salt and the or-

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ganic epoxide (for this reaction, one equivalent of an epoxide is the same as one mole thereof). This is not to say that complexes made from one equivalent of the polyvalent metal salt and less than or more than one equivalent of the organic epoxide are unsuited for the purpose of this invention. Complexes prepared using as little as 0.1 or 0.25 equivalent or as much as 1.5 or 2 or more equivalents of the organic epoxide per equivalent of polyvalent metal salt are satisfactory for the purpose of this invention. For reasons of economy and optimum corrosion inhibition, however, it is generally preferred to use about equivalent amounts of the two starting materials.

The reaction between the organic epoxide and the polyvalent metal salt of the acid phosphate esters is only slightly exothermic, so in order to insure complete reaction some heat is generally supplied to the reaction mass. The time and temperature for this reaction are not particularly critical; satisfactory results may be obtained by maintaining the mass for 0.5–6 hours at a temperature within the range of from about 40° C. to about 150° C. Ordinarily, the product is clear and does not require a filtration. In some instances, however, it may be desirable to filter the product, particularly when the polyvalent metal salt starting material has not been purified.

The following examples are offered to illustrate specific modes of carrying out the process of this invention. All parts are by weight unless otherwise indicated.

Example 1

49 parts (0.73 equivalent) of dipropylene glycol, 95 parts (0.73 equivalent) of isooctyl alcohol, and 133 parts of aromatic petroleum spirits boiling in the range 316°–349° F. are introduced into a reaction vessel. The whole is stirred at room temperature and 60 parts (0.42 mole) of phosphorus pentoxide is introduced portionwise over a period of about 0.5 hour. The heat of reaction causes the temperature to rise to about 80° C. After all of the phosphorus pentoxide has been added, the whole is stirred for an additional 0.5 hour at 93° C. The resulting acid phosphate esters show an acid number of 91 with bromphenol blue as an indicator.

The mixture of acid phosphate esters is converted to the corresponding zinc salt by reacting it with 34.5 parts of zinc oxide for 2.5 hours at 93° C. Thereafter 356 parts (one equivalent per equivalent of zinc salt) of butyl epoxystearate is added to the zinc salt at 88° C. over a period of about one hour and the whole is stirred for 4 hours at 90° C. Filtration of the mass yields 684 parts of a zinc-containing organic phosphate complex having the following analysis:

Phosphorus	percent	3.55
Zinc	do	3.78
Specific gravity		1.009

Example 2

A cadmium-containing organic phosphate complex is made in the manner set forth in Example 1, except that 54.5 parts of cadmium oxide is used in lieu of the specified amount of zinc oxide.

Example 3

A lead-containing organic phosphate complex is made in the manner set forth in Example 1, except that 95 parts of lead monoxide is used in lieu of the specified amount of zinc oxide.

Example 4

A barium-containing organic phosphate complex is made in the manner set forth in Example 1, except that 73 parts of barium hydroxide is used in lieu of the specified amount of zinc oxide.

Example 5

A tin-containing organic phosphate complex is made in the manner set forth in Example 1, except that 57 parts

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of stannic oxide is used in lieu of the specified amount of zinc oxide.

Example 6

520 parts (4 equivalents) of isooctyl alcohol, 268 parts of dipropylene glycol (4 equivalents), and 1031 parts of toluene solvent are introduced into a reaction vessel. The whole is stirred and 243 parts (1.71 moles) of phosphorus pentoxide is added portionwise over a period of 2 hours. The exothermic character of the reaction causes the temperature to rise from room temperature to 60° C. To insure complete reaction, the whole is stirred for an additional 4 hours at 60° C. The resulting 50% solution of the acid phosphate esters in toluene shows an acid number of 88 with bromphenol blue as an indicator.

1000 parts of the toluene solution of acid esters is converted to the corresponding zinc salt by reaction with 83 parts of zinc oxide for 5.5 hours at 40–45° C. Filtration yields a clear, light-yellow toluene solution of the zinc salt. 360 parts of this toluene solution (containing 0.34 equivalent of zinc salt) is heated with 25 parts (0.34 equivalent) of beta-propiolactone for 5.5 hours at 50–60° C. to yield the desired zinc-containing organic phosphate complex as a 55% solution in toluene. It has the following analysis:

	Percent
Phosphorus	4.26
Zinc	5.05

Example 7

A toluene solution of acid phosphate esters is made in the manner set forth in Example 6.

994 parts of the indicated toluene solution of acid phosphate esters is heated with 76 parts of calcium hydroxide for 5 hours at 45–60° C. Filtration yields the calcium salt of the acid phosphate esters as a 51% solution in toluene.

325 parts (0.52 equivalent) of the toluene solution of the calcium salt is heated with 220 parts (0.52 equivalent) of 85% butyl epoxystearate for 5 hours at 50–60° C. to prepare the desired calcium-containing organic phosphate complex as a 71% solution in toluene. It has the following analysis:

	Percent
Phosphorus	2.34
Calcium	1.65

Example 8

A calcium-containing organic phosphate complex is made in the manner set forth in Example 7, except that 38 parts (0.52 equivalent) of beta-propiolactone is used in lieu of the butyl epoxystearate. The product has the following analysis:

	Percent
Phosphorus	3.74
Calcium	2.75

Example 9

A batch of acid phosphate esters is made in the manner set forth in Example 6, except that the amount of toluene solvent employed is reduced to 443 parts so as to yield a more concentrated (70%) solution of the esters in toluene.

290 parts of this toluene solution is neutralized with a mixture of 28.2 parts of zinc oxide and 11.2 parts of calcium hydroxide for 3 hours at 50–70° C. Filtration of the mass yields a mixed zinc-calcium salt of the acid phosphate esters as a 73% solution in toluene.

116.2 parts of the mixed zinc-calcium salt (0.19 equivalent) and 80.4 parts (0.19 equivalent) of 85% butyl epoxystearate are heated for 6 hours at 50–60° C. to prepare an 84% solution in toluene of a calcium and zinc-containing organic phosphate complex. It shows the following analysis:

	Percent
Phosphorus -----	2.69
Calcium -----	0.22
Zinc -----	3.13

Example 10

A zinc-containing organic phosphate complex is made in the manner set forth in Example 1, except for the following differences: 58 parts of 1,2-propylene oxide is used in lieu of the butyl epoxystearate and the reaction between the zinc salt of the acid phosphate esters and the 1,2-propylene oxide is carried out at 30°–35° C. rather than 88–90° C.

Example 11

A zinc-containing organic phosphate complex is made in the manner set forth in Example 1, except that 136 parts (0.73 equivalent) of lauryl alcohol and 39 parts (0.73 equivalent) of diethylene glycol are used in lieu of the specified amounts of isooctyl alcohol and dipropylene glycol.

Example 12

A zinc-containing organic phosphate complex is made in the manner set forth in Example 1, except that 185 parts (1.17 equivalents) of n-decanol-1 and 7.9 parts (0.29 equivalent) of pentaerythritol are used in lieu of the specified amounts of isooctyl alcohol and dipropylene glycol.

The novel, metal-containing organic phosphate complexes of this invention are principally useful, as indicated, to provide corrosion protection for metal surfaces. To accomplish this purpose, the metal surfaces are provided with a thin film of the complex, which film varies from about 10 to about 500 milligrams and preferably from about 100 to about 400 milligrams per square foot of surface area. Such films may be applied to the metal surface by any of the ordinary techniques used in the paint industry such as, e.g., brushing, spraying, dipping, or roller-coating. Depending on the particular mode of application selected, the complex may be thinned by means of a solvent such as, e.g., petroleum aromatic spirits, benzene, toluene, and the like to a viscosity best suited for such mode of application. In dipping operations, for example, 50% solutions of the complexes in toluene or aromatic petroleum spirits have been found to yield a film which, when dry, ranges from about 250 to about 350 milligrams per square foot of surface area.

The complexes of this invention are useful in retarding the corrosion of many kinds of metals, including iron, steel, ferrous alloys, zinc, aluminum, cadmium, and magnesium. They are particularly effective, however, in extending the life of the so-called "phosphated" metal surfaces, i.e., surfaces which have been treated with an aqueous inorganic phosphate solution to form thereon an integral, adherent inorganic phosphate coating. Such coatings are widely used in the automotive and appliance industries as bases to insure good adhesion of decorative top-coats such as paint, enamel, varnish, alkyd resins, epoxy resins, and the like. Generally these inorganic phosphate coatings have inadequate corrosion resistance, i.e., not much better than that of the bare metal. As a consequence, a phosphated metal surface is very susceptible to corrosion before the desired decorative top-coat is applied thereto. The metal fabricating and finishing industries have long sought a treatment or a material which would protect phosphated metal parts, particularly phosphated ferrous metal parts, against corrosion to a degree great enough to allow them to be stored outdoors. Thin films of the complexes of the present invention have provided an answer to this problem by extending the anti-corrosion life of phosphated ferrous metal parts several hundred-fold.

It is believed unnecessary to lengthen the present specification unduly by a recitation of the many ways in which a metal surface may be phosphated. The literature is replete with patents, e.g., U.S. Patent Numbers 1,206,075; 1,247,668; 1,305,331; 1,485,025; 1,610,362; 1,980,518, and 2,001,754, which describe the preparation and use of aqueous inorganic phosphating solutions. A particularly useful class of aqueous phosphating solutions for preparing phosphated metal surfaces which show excellent response to the metal complexes of this invention is described in U.S. application Serial No. 373,449, filed August 5, 1953, now U.S. Patent No. 3,090,709 by John A. Henricks. The aqueous phosphating solutions of Henricks contain as essential ingredients zinc ion, phosphate ion, nitrate ion, and calcium ion. They produce an integral, tightly-adherent micro-crystalline or amorphous phosphate coating on metals which is highly desirable as a paint base.

The complexes of this invention are also useful in preventing or retarding the so-called "white corrosion" of zinc, zinc alloys, and galvanized (i.e., zinc-coated) steel. They are also effective in increasing the life of electroplated zinc or electroplated cadmium surfaces. They are also useful as corrosion-inhibiting ingredients in metallic paints such as, e.g., aluminum paints or zinc-filled paints.

The utility of the complexes of the present invention in retarding corrosion is shown by the results obtained in a Salt Fog Corrosion test.

A number of 4-inch x 8-inch panels of clean, solvent degreased, 20-gauge SAE 1020 cold-rolled steel prepared according to ASTM procedure D-609-52 were spray-phosphated for about 70 seconds at 160–165° F. with an aqueous phosphating solution containing 0.15% zinc ion, 0.54% phosphate ion, 0.39% calcium ion, and 1.4% nitrate ion. Thereafter, they were sprayed for about 30 seconds at 70° F. with a 0.01% aqueous solution of chromic acid, water-rinsed, and dried.

Several sets of three panels each were then assembled and/or further treated as shown in Table I:

TABLE I

Panel Set:	Description
A -----	Clean, solvent-degreased panels.
B -----	Phosphated panels.
C -----	Phosphated panels containing a protective film of 310 ± 10 mg./square foot of a commercial zinc phosphorodithioate inhibitor. ¹
D -----	Phosphated panels containing a protective film of 310 ± 10 mg./square foot of the complex of Example 1. ²

¹ The commercial inhibitor was obtained as a 40% solution in toluene. Each panel was dip-coated therein and allowed to air dry.

² The complex of Example 1 (an 80% solution in toluene) was diluted with more toluene to yield a 50% solution. Each panel was dip-coated therein and allowed to air-dry.

Each set of panels was then subjected to the Salt Fog Corrosion test described in ASTM procedure B117-57T. This test employs a chamber in which a mist or fog of 5% aqueous sodium chloride is maintained in contact with the panels at $95 \pm 2^\circ$ F. In the present instance, the panels were inspected each 0.5 hour of the first six hours for the development of rust on the flat areas (edges disregarded) of the panels. Thereafter, inspection was made daily. At the first sign of rust on a flat area, the panel was removed and the time which had elapsed since the beginning of the test was recorded as the "Fail Time" for that panel.

The results obtained on panel sets A through D are shown in Table II:

TABLE II

Panel Set	Fail Time, hours	Average Fail Time, hours
A -----	0.5 0.5 0.5	0.5
B -----	0.5 1.0 213	0.8
C ¹ -----	264 264 477	247
D ² -----	357 357	397

¹ Panels in this set had an objectionable odor after removal from the Salt Fog chamber.

² Panels were odor-free.

It will be noted that panel set D (processed according to the present invention) offered a significant improvement in corrosion life over that observed for panel set C (processed by known methods). In addition, the panels processed according to the present invention did not develop an objectionable odor after having been in contact with the warm, humid atmosphere of the Salt Fog chamber.

What is claimed is:

1. A method for inhibiting the corrosion of a metal surface which comprises applying to said surface a film of a metal-containing organic phosphate complex prepared by the process which comprises the reaction of:

(A) a polyvalent metal salt selected from the group consisting of zinc, cadmium, lead, iron, cobalt, nickel, barium, calcium, strontium, magnesium, copper, bismuth, tin, chromium, and manganese salts of the acid phosphate esters derived from the reaction of phosphorus pentoxide with a mixture of a monohydric alcohol selected from the group consisting of saturated aliphatic and cycloaliphatic alcohols containing from about 3 to about 18 carbon atoms, and from 0.25 to 4.0 equivalents of a polyhydric alcohol having from 2 to about 4 hydroxyl groups and containing from about 2 to about 41 carbon atoms, with

(B) at least about 0.1 equivalent of an organic epoxide containing from about 2 to about 57 carbon atoms and selected from the group consisting of epoxy alkanes, epoxy alkyl carboxylic acids, lactones, styrene oxide, and alpha-methyl styrene oxide.

2. A method in accordance with claim 1 wherein the monohydric alcohol of (A) is an alkanol.

3. A method in accordance with claim 1 wherein the monohydric alcohol of (A) is an octyl alcohol,

4. A method in accordance with claim 1 wherein the monohydric alcohol of (A) is isooctyl alcohol.

5. A method in accordance with claim 1 wherein the polyhydric alcohol of (A) is a glycol.

6. A method in accordance with claim 1 wherein the polyhydric alcohol of (A) is propylene glycol.

7. A method in accordance with claim 1 wherein the polyhydric alcohol of (A) is dipropylene glycol.

8. A method in accordance with claim 1 wherein the polyvalent metal salt of (A) is a zinc salt.

9. A method in accordance with claim 1 wherein the organic epoxide of (B) is an epoxy alkane.

10. A method in accordance with claim 1 wherein the organic epoxide of (B) is an epoxy alkane containing from about 12 to about 57 carbon atoms.

11. A method in accordance with claim 10 wherein the organic epoxide of (B) contains a carboxylic ester group.

12. A method for inhibiting the corrosion of a metal surface which comprises applying to said surface a film of a metal-containing organic phosphate complex prepared by the process which comprises the reaction of:

(A) a zinc salt of the acid phosphate esters derived from the reaction of phosphorus pentoxide with a mixture of isooctyl alcohol and dipropylene glycol with

(B) at least about 0.1 equivalent of butyl epoxy-stearate.

13. A method in accordance with claim 1 wherein the metal surface is a phosphated metal surface.

14. A method in accordance with claim 1 wherein the metal surface is a phosphated ferrous metal surface.

15. A metal article the metal surface of which has been inhibited against corrosion in accordance with the method of claim 1.

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