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3,207,611

COATING COMPOSITION

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The present invention relates to a fluid composition adapted to provide an electrically conductive, protective coating for meals. In a more particular sense, it relates to a fluid composition adapted to provide a weldable protective coating for ferrous metals.

It is common practice in the automotive industry to coat various ferrous undercarriage parts of passenger cars and trucks such as brackets, box-channels, panels, and braces with a suspension of zinc dust in an organic vehicle, generally an alkyd or synthetic resin. Some manufacturers depart from this practice in that they prefer to coat ferrous metal stock with the zinc-filled organic vehicle before it is formed into the various parts. In any event, they all seek to provide these ferrous parts with a coating which protects the parts from corrosion and which, at the same time, does not impair the weldability of the coated ferrous surface.

The zinc-filled organic vehicles, i.e., "zinc-filled paints," presently available for this purpose have not been fully satisfactory. They have afforded only limited protection against corrosion although they have been satisfactory with respect to weldability. In an effort to improve corrosion resistance, some manufacturers have first treated the ferrous parts and/or ferrous stock from which the parts are made with an aqueous phosphating solution to form thereon an integral inorganic phosphate coating and thereafter applied a zinc-filled paint over the phosphate coating. Although a significant improvement in corrosion resistance is obtained by such a two-step procedure, the increased handling and processing costs have seriously limited its wide-spread application.

It is an object of the present invention to provide a fluid composition which forms a protective, adherent, easily weldable coating on metal surfaces.

Another object is to provide a composition particularly adapted to prevent the corrosion of ferrous metal surfaces.

Still another object is the provision of corrosion-resistant, weldable ferrous articles.

According to the present invention these and other objects are achieved by means of a fluid composition adapted to form a protective coating on metals which contains as essential ingredients:

(A) Finely divided zinc,

(B) A metal-containing organic phosphate complex prepared by the process which comprises the reaction of

(I) A polyvalent metal salt of the acid phosphate esters derived from the reaction of a phosphorus-containing reagent selected from the group consisting of phosphorus pentasulfide and phosphorus pentoxide with a mixture of monohydric and polyhydric alcohols, and

(II) At least about 0.1 equivalent of an organic epoxide, and

(C) A metal-free organic phosphate complex prepared by the process which comprises mixing one mole of phosphorus pentoxide, from about 0.2 to about 12.5 moles of a copolymer of allyl alcohol and a styrene, and from about 0.3 to about 5.0 moles of an alkyl phenol, and heating said mixture at a temperature within the range from about 75° C. to about 150° C.

In addition to these characterizing ingredients, the fluid composition will also generally contain a viscosity-reducing amount of a volatile solvent and a pigment-suspending

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agent such as castor wax or a polyvalent metal stearate to prevent the settling and agglomeration of the zinc dust into a hard, difficultly-dispersible precipitate. For obvious practical reasons, then, it is generally highly desirable to include both a pigment-suspending agent and a volatile solvent in the fluid compositions of this invention.

INGREDIENT (A)

Ingredient (A), the finely-divided zinc, is preferably commercial powdered zinc passing 325-mesh screen according to ASTM test E 11-58T. Powdered zinc of such fineness is more readily dispersed with the other ingredients of the composition than is a coarser grade and, furthermore, shows less tendency to precipitate upon storage.

INGREDIENT (B)

Ingredient (B), the metal-containing organic phosphate complex prepared by the reaction of an organic epoxide with a polyvalent metal salt of the acid phosphate esters derived from the reaction of phosphorus pentasulfide and/or phosphorus pentoxide with a mixture of monohydric and polyhydric alcohols, is described in detail in U.S. Patent 2,820,723 to W. M. Le Suer and in co-pending application Ser. No. 139,845, filed September 22, 1961. In the interest of not unduly lengthening the present application it is intended that the entire disclosures of the aforesaid patent and pending application be incorporated herein by reference. It should also be noted that the term "phosphate" as used herein is intended to be generic to both oxyphosphates and phosphorothioates.

The patent to Le Suer is concerned with the reaction of an organic epoxide with a metal phosphorodithioate, especially a zinc phosphorodithioate derived from the neutralization of a phosphorodithioic acid prepared from the reaction of phosphorus pentasulfide with a mixture of monohydric and polyhydric alcohols.

Application Ser. No. 139,845 describes a metal-containing organic phosphate complex prepared by the reaction of an organic epoxide with a polyvalent metal salt of the acid oxyphosphate esters derived from the reaction of phosphorus pentoxide with a mixture of monohydric and polyhydric alcohols.

The monohydric alcohols useful in the preparation of ingredient (B) 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, methylcyclohexyl, octyl, isooctyl, decyl, lauryl, tridecyl, oleyl, benzyl, betaphenethyl, alpha-pyridylethyl, etc., alcohols. In some instances it is also desirable to use aromatic alcohols, i.e., phenols, such as, e.g., phenol, cresol, tertiary-butylphenol, isooctylphenol, and the like. 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 ingredient (B) 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, sulfides, 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, monophenyl ether of glycerol, mono-benzyl ether of glycerol, 1,3,5-hexanetriol, pentaerythritol, sorbitol dioctanoate, pentaerythritol dioleate, and the like. In some instances,

it is also desirable to use polyhydric aromatic alcohols, i.e., polyhydric phenols, such as, for example, hydroquinone, catechol, and the various alkylidene bisphenols such as, e.g., 4,4'-methylene bisphenol, 4,4'-propylidene bisphenol, and the like.

The alcohol mixture may contain a single monohydric and a single polyhydric alcohol, or a plurality of one or 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 term "equivalent" as used herein reflects the hydroxyl equivalency of the alcohol. Thus, for example, one mole of octyl alcohol is one equivalent thereof, one mole of ethylene glycol is two equivalents thereof, one mole of glycerol is three equivalents thereof, etc. The use of mixtures outside of this range tends to produce either intractable esters, or esters which, when converted in ingredient (B), are deficient in film-forming properties. Mixtures of isooctyl 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 and/or phosphorus pentasulfide 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 from about 40° C. to about 200° C. are most satisfactory. When phosphorus pentasulfide is used the temperature is preferably kept below 140° C. to avoid decomposition of the acid thioesters formed. Such precautions are not necessary when phosphorus pentoxide is used since the acid oxyesters formed are much less susceptible to decomposition than the acid thioesters. The reaction time required varies according to the temperature, the phosphorus-containing reagent employed, and the hydroxyl activity of the alcohol mixture. 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 and/or phosphorus pentasulfide 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 permitted 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 fluid compositions of this invention to metal surfaces.

The reaction of phosphorus pentasulfide with alcohols or phenols is known to produce organic phosphorodithioic acids. The stoichiometry of this reaction is likewise well-known; it involves the reaction of one mole of phosphorus pentasulfide with 4 equivalents of an alcohol or mixture of alcohols. Lesser or greater amounts of alcohol can be used, e.g., from about 2 to about 6 or more equivalents, but in such instances there is generally either incomplete reaction or an excess of the alcohol remains as the diluent in the product. For the purpose of the present invention, it is contemplated to use from about 2 to about 6 or more equivalents of alcohol per mole of phosphorus pentasulfide, although it is usually preferred to use the stoichiometric proportions of 4 equivalents to 1 mole, respectively, in the interest of convenience and economy.

The reaction of phosphorus pentoxide with alcohols is

known to produce a mixture of oxyphosphate esters consisting principally of acid oxyphosphate esters of the general formula:



where x equals one or two and R is an organic radical, although some neutral triesters of the formula $(RO)_3PO$ may also be formed. The stoichiometry of this reaction is not clear; no equation can be given which indicates the precise nature and amounts of the acid oxyphosphate esters formed. In any event, a complex mixture of different esters is always obtained, the relative proportions of which can be altered by varying the amount of alcohol used from about 2 to about 6 or more equivalents per mole of phosphorus pentoxide. 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.

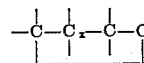
In lieu of either phosphorus pentoxide or phosphorus pentasulfide, a mixture thereof may be used in reaction with the mixture of monohydric and polyhydric alcohols. In such instances, a complex mixture of acid esters of both oxyphosphoric and phosphorodithioic acids results. The use of phosphorus oxysulfides such as, e.g., $P_4O_6S_4$, is likewise contemplated since they are deemed to be the equivalent of mixtures of P_2S_5 and P_2O_5 for the purpose of this invention.

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 ingredient (B) 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 for the preparation of ingredient (B) of the present invention is the zinc salt of the acid oxyphosphate esters formed by the reaction of a mixture of equivalent amount of isooctyl alcohol and dipropylene glycol with phosphorus pentoxide. Another related and highly effective starting material is prepared in the same manner, except that phosphorus pentasulfide is used in lieu of phosphorus pentoxide.

The formation of the metal-containing organic phosphate complex used as ingredient (B) of this invention involves, as indicated, a reaction between the polyvalent metal salt of certain acid phosphate esters and an organic epoxide. The organic epoxides, i.e., compounds containing at least one



linkage where x is zero or a small integer, suitable for the preparation of ingredient (B) include the various substituted and unsubstituted alkyline 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, methylcyclohexene oxide, 1,2;11,12-diepoxydodecane, styrene oxide, alpha-methyl styrene oxide, beta-propiolactone, methyl epoxy-caprylate, 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 three carbon atoms.

Especially preferred are those epoxides which contain at

least 12 carbon atoms and also a carboxylate group in the molecule. Thus, the commercially available epoxidized carboxylic ester, butyl epoxystearate, and epoxidized soyabean oil are very satisfactory epoxides for the preparation of ingredient (B). The low molecular weight carboxylic acid-epoxide, beta-propiolactone, is likewise useful for the preparation of ingredient (B) herein, especially when it is used in combination with a high molecular weight epoxide such as, e.g., butyl epoxystearate. 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 with the organic epoxide to form the metal-containing organic phosphate complex used as ingredient (B) herein is not precisely known. There are indications, however, that the reaction involves about one equivalent each of the polyvalent metal salt and the organic 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 to 2 or more equivalents of the organic epoxide per equivalent of polyvalent metal salt are satisfactory for use as ingredient (B). For reasons of economy and optimum corrosion inhibition, however, it is usually pre-

Table 1

Example No. of U.S. 2,820,723	Metal containing organic phosphate derived from—			
	Zinc salt of the phosphorodithioic acid prepared from the reaction of P_2S_5 with—	Equivalents	Organic epoxide	Equivalents
10	1----- Equivalent amounts of iso-octyl alcohol and propylene glycol.	1.0	Butylene oxide	1.0
	2----- do-----	1.0	Butyl epoxystearate.	1.0
	3----- A 1:3 equivalent mixture of iso-octyl alcohol and propylene glycol.	1.0	Butylene oxide	1.0
15	4----- do-----	1.0	Butyl epoxystearate.	1.0
	5----- Equivalent amounts of iso-octyl alcohol and ethylene glycol.	1.0	Dodecene oxide	1.0
20	6----- do-----	1.0	Epoxyamyl propyl sulfide.	1.0
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Specific examples of metal-containing organic phosphate complexes which are disclosed in detail in application Ser. No. 139,845 and which are also useful as ingredient (B) herein are shown in Table 2.

Table 2

Example No. in Ser. No. 139,845	Metal-containing organic phosphate complex derived from—				
	Metal salt of oxyphosphate acid esters			Organic epoxide	Equivalents
	Acid esters derived from reaction of P_2O_5 with—	Metal	Equivalents		
1-----	Equivalent amounts of iso octyl alcohol and dipropylene glycol.	Zn-----	1.0	Butyl epoxystearate---	1.0
2-----	do-----	Cd-----	1.0	do-----	1.0
3-----	do-----	Pb-----	1.0	do-----	1.0
4-----	do-----	Ba-----	1.0	do-----	1.0
5-----	do-----	Sn-----	1.0	do-----	1.0
6-----	do-----	Zn-----	0.34	Beta-propiolactone---	0.34
7-----	do-----	Ca-----	0.52	Butyl epoxystearate---	0.52
8-----	do-----	Ca-----	0.52	Beta-propiolactone---	0.52
9-----	do-----	Zn and Ca---	0.19	Butyl epoxystearate---	0.19
10-----	do-----	Zn-----	1.0	1,2-propylene oxide---	1.0
11-----	Equivalent amounts of lauryl alcohol and diethylene glycol.	Zn-----	1.0	Butyl epoxystearate---	1.0
12-----	A 4:1 equivalent mixture of n-decanol-1 and pentaerythritol.	Zn-----	1.0	do-----	1.0

ferred 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 from about 40° C. to about 150° C. Ordinarily, the product is clear and does not require a filtration. In some instances, however, it is desirable to filter the product, particularly when the polyvalent metal salt of the acid phosphate esters has not been purified previously.

Specific examples of metal-containing organic phosphate complexes which are disclosed in detail in U.S. Patent 2,820,723 and which are useful as ingredient (B) herein are shown in Table 1.

Additional examples of metal-containing organic phosphate complexes useful as ingredient (B) herein are as follows:

EXAMPLE B-1

In a flask equipped with a stirrer, 576 parts (3 moles) of heptylphenol and 114 parts (0.5 mole) of 2,2-bis-(para-hydroxyphenyl)propane are introduced and heated to 120° C. While the whole is stirred vigorously, 222 parts (1 mole) of P_2S_5 is added gradually over a period of 3 hours and heating is continued for an additional 3 hours. Filtration of the mass yields the complex phosphorodithioic acid, which is diluted with an equal weight of toluene to facilitate handling.

1376 parts of the toluene solution of the acid is mixed with 75 parts of zinc oxide and 5 parts of water. The whole is heated for 5 hours at 60-65° C. and then filtered to yield a filtrate which is a 51.2 percent solution of the zinc phosphorodithioate in toluene. Treatment of this

zinc phosphorodithioate with an equivalent amount (658 parts) of butyl epoxystearate for 2 hours at 50–60° C. yields the desired zinc-containing organic phosphate complex in solution in toluene.

EXAMPLE B-2

A mixture of 520 parts (4.0 equivalents) of isooctyl alcohol and 268 parts (4.0 equivalents) of dipropylene glycol is reacted with 385 parts (1.73 moles) of phosphorus pentasulfide for 8 hours at 60–68° C. The resulting phosphorodithioic acid (1,110 parts) is diluted with 1,570 parts of benzene and neutralized with a 5 percent excess of zinc oxide (147 parts) for 7 hours under reflux, the water of neutralization being removed as formed by means of a side-arm water trap. Filtration yields 2,710 parts of a benzene solution of the zinc phosphorodithioate, from which benzene is removed by heating to 93° C./50 mm. Hg. The substantially benzene-free zinc phosphorodithioate (1,235 parts) is blended with 250 parts of aromatic petroleum spirits boiling in the range 316–349° F. and then mixed with an equivalent amount (1,425 parts) of butyl epoxystearate over a one hour period at 40–50° C. The resulting zinc-containing organic phosphate complex has the following analysis:

Phosphorus -----	percent--	3.65
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EXAMPLE B-3

A mixture of 520 parts (4.0 equivalents) of isooctyl alcohol and 268 parts (4.0 equivalents) of dipropylene glycol in 1,031 parts of toluene is introduced into a flask and 243 parts (1.71 moles) of phosphorus pentoxide is introduced portionwise over a period of 2 hours. The exothermic nature of the reaction causes the temperature of the mass to rise to about 60° C. Thereafter, the whole is heated for 4 hours at 60° C. to yield the desired oxyphosphate esters as a 50 percent solution in toluene.

1000 parts of the aforesaid toluene solution is reacted with 83 parts of zinc oxide and 5 parts of water for 5.5 hours at 40–45° C. Filtration of the mass yields 1,050 parts of the desired zinc-containing organic phosphate as a 52.4 percent solution in toluene. 390 parts (0.59 equivalent) of the toluene solution of the zinc-containing organic phosphate is reacted with 422 parts (0.53 equivalent) of 85 percent butyl epoxystearate over a 6-hour period at 50–60° C. Filtration of the reaction mass yields the desired zinc-containing organic phosphate complex as a 69.7 percent solution in toluene. It shows the following analysis:

	Percent
Phosphorus -----	2.3
Zinc -----	2.04

EXAMPLE B-4

360 parts (0.54 equivalent) of the toluene solution of the zinc-containing organic phosphate described in Example B-3 is reacted with 25 parts (0.35 equivalent) of beta-propiolactone for 5.5 hours at 50–60° C. Filtration of the reaction mass yields the desired zinc-containing organic phosphate complex as a 55.4 percent solution in toluene. It shows the following analysis:

	Percent
Phosphorus -----	4.26
Zinc -----	5.05

INGREDIENT (C)

Ingredient (C), the metal-free organic phosphate complex, is described in detail in co-pending application Ser. No. 50,844, filed August 22, 1960. In brief, this ingredient is prepared by mixing one mole of phosphorus pentoxide, from about 0.2 to about 12.5 moles of a copolymer of allyl alcohol and a styrene, and from about 0.3 to about 5.0 moles of an alkylphenol, and heating said mixture at a temperature within the range from about 75° C. to about 150° C.

Ordinarily the reaction is carried out in a solvent and the solvent then removed, if desired, by distillation when

the reaction is completed. Suitable solvents for this reaction include, e.g., xylene, benzene, cyclohexane, chlorobenzene, ethylene dichloride, and dioxane. Other inert, relatively volatile solvents (so as to afford easy removal from the product mixture) may also be used. The reaction may also be carried out in the absence of a solvent and in such cases there is the obvious advantage of not having to remove the solvent when the reaction is completed.

The reaction of the process appears to involve first a reaction between phosphorus pentoxide and the copolymer of allyl alcohol and a styrene, followed then by reaction of this intermediate product with the alkylphenol. Presumably this latter reaction is a transesterification. The reaction mixture is at first cloudy and viscous, but as it proceeds the cloudiness and viscosity disappear and the final product mixture is a relatively clear solution. The optimum reaction time is about 4 to 6 hours, although a suitable product can be obtained at any point within a period of from about 1 to about 10 hours.

The copolymer of allyl alcohol and a styrene preferably is a low molecular weight copolymer prepared from an approximately equimolar mixture of the two monomers. The molecular weight of the copolymer should be within the range from about 750 to about 1,500, preferably about 1,100–1,150. The styrene monomer may be styrene itself, and most usually it is, or it may be any of the various substituted styrenes such as monochloro styrene, alkyl-substituted styrene, and alpha-substituted styrenes in which latter the substituent is an alkyl group, preferably a methyl group.

The alkylphenol reactant may be either 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-alkyl phenol in which the alkyl group contains from 1 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-ethyl phenols; para-isopropylphenol, para-tertiary butylphenol, para-tertiary amylphenol, heptylphenol, diisobutylphenol, n-decylphenol, wax alkylated alpha-naphthol, wax-alkylated phenol, and polyisobutene-substituted phenol in which the polyisobutene substituent contains from about 20 to about 75 carbon atoms. The alkylphenol may also contain substituent groups such as, e.g., chloro, fluoro, nitro, alkoxy, sulfide, nitroso, etc.

The process is carried out simply by mixing the specified reactants, preferably with a solvent, and heating the resulting solution at a temperature within the range from about 75° C. to about 150° C. until the reaction is complete. As indicated earlier, the first stages of the overall reaction produce a cloudy, thickened reaction mixture and as the reaction proceeds this is changed to a relatively clear, non-viscous solution. Several illustrative examples follow:

EXAMPLE C-1

A mixture of 1,412 parts (1.2 moles) of a 1:1 molar copolymer of allyl alcohol and styrene having an average molecular weight of about 1,100 and available commercially under the trade designation "Polyol X-450," 168 parts (1.0 mole) of para-tertiary amylphenol, 68 parts (0.5 mole) of phosphorus pentoxide, and 1,648 parts of xylene solvent is prepared at room temperature and then heated at the reflux temperature, ca. 141° C., for 6 hours. The reaction mixture is stirred throughout this period and water of reaction is removed by means of a side-arm water trap. At the end of this time the xylene is removed by distillation to yield a plastic, non-viscous mass. This residue, while still hot, i.e., about 100° C., is diluted with 824 parts of isobutyl alcohol. The product, a 65 percent solution of the metal-free organic phos-

phate complex in isobutyl alcohol, shows the following analysis:

Phosphorus -----percent-- 1.16
Acid No. (phenolphthalein indicator) ----- 22.6

EXAMPLE C-2

A mixture of 313 parts (0.284 mole) of Polyol X-450, 314 parts (0.786 mole) of mono-(polyisobutene-substituted)phenol wherein the polyisobutene substituent contains an average of about 22 carbon atoms, 31 parts (0.218 mole) of phosphorus pentoxide, and 660 parts of xylene is heated to the reflux temperature, ca. 140° C., and maintained at this temperature for 6 hours while water is removed by means of a side-arm water trap. Substantially all of the xylene is removed by distillation of the mass at 140° C./20 mm. Hg. and then the residue is diluted with 350 parts of isobutyl alcohol. The product, a 65 percent solution of the metal-free organic phosphate complex in isobutyl alcohol, shows the following analysis:

Phosphorus -----percent-- 1.35
Acid No. (bromphenol blue indicator) ----- 16.7

Additional examples of metal-free organic phosphate complexes are shown in Table 3. They are prepared in the same manner set forth in Example C-2 using the indicated quantities of reagents.

Table 3

Example No.	Moles of the indicated starting materials employed			
	Polyol X-450	Alkylphenol		Phosphorus pentoxide
		Identity	Moles	
C-3-----	0.87	Para-tertiary amylphenol	16.2	4
C-4-----	0.8	do.	12	4
C-5-----	1.8	do.	12	4
C-6-----	5	Heptylphenol	12	4
C-7-----	5	Para-cresol	12	4
C-8-----	5	Nonylphenol	12	4

For the purposes of the present invention, it is also desirable in certain instances, to acylate ingredient (C) with a high molecular weight unsaturated aliphatic carboxylic acid containing at least 12 carbon atoms and/or ester thereof such as, e.g., linoleic acid, linolenic acid, linseed oil, tung oil, tung oil acids, methyl linoleate, ethyl linolenate, chloroleic acid, phenyloleic acid, oleic acid, behenic 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 which contain at least two double bonds such as linoleic and linolenic acids.

The acylation can be carried out in any one of several ways such as, for example: adding the unsaturated aliphatic carboxylic acid and/or ester thereof to the reaction mixture prepared for ingredient (C) and then carrying out the reaction in the manner indicated earlier; heating the copolymer or allyl alcohol and a styrene with the unsaturated aliphatic carboxylic acid and/or ester thereof for 0.5-12 hours at 80-200° C. in the presence, optionally, of an esterification catalyst and then using such acylated copolymer as the polymeric reactant in the preparation of ingredient (C); or heating the unsaturated aliphatic carboxylic acid and/or ester with ingredient (C) for 0.5-12 hours at 80-200° C.

In each of the foregoing procedures, the amount of the unsaturated aliphatic carboxylic acid and/or ester used should be within the range from about 0.5 to about 4 moles, preferably from about 1.0 to about 3 moles, per mole of the copolymer of allyl alcohol and a styrene.

The following examples set forth specific modes of preparing an acylated ingredient (C). The acid no. in each instance is determined using bromphenol blue as an indicator.

EXAMPLE C-9

431 parts (0.375 mole) of Polyol X-450, 140 parts (0.5 mole) of linoleic acid, and 0.2 part of para-toluene sulfonic acid (esterification catalyst) are dissolved in 864 parts of xylene. The whole is refluxed for 6 hours and the water of esterification is removed by means of a side-arm water trap. To the resultant acylated Polyol X-450 in xylene are added 231 parts (1.41 moles) of para-tertiary amylphenol and 71 parts (0.5 mole) of phosphorus pentoxide. The reaction mixture is heated for 6 hours at the reflux temperature to yield the desired acylated, metal-free, organic phosphate complex as a 50 percent solution in xylene. It shows the following analysis:

Phosphorus -----percent-- 1.86
Acid No. ----- 36

EXAMPLE C-9A

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 amylphenol, 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 analysis.

Phosphorus -----percent-- 1.28
Acid No. ----- 98

EXAMPLE C-10

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 amylphenol, 71 parts (0.5 mole) of phosphorus pentoxide, and 1278 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 analysis.

Phosphorus -----percent-- 1.15
Acid No. ----- 84

EXAMPLE C-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 1408 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 analysis.

Phosphorus -----percent-- 0.99
Acid No. ----- 72

EXAMPLE C-12

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 phosphorus 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 prod-

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

Phosphorus -----percent-- 1.14
Acid No. ----- 124

EXAMPLE C-13

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 analysis.

Phosphorus -----percent-- 1.02
Acid No. ----- 51

Each of the characterizing ingredients (A), (B), and (C) are essential in preparing the fluid compositions of the present invention. In addition to these characterizing ingredients, it is generally desirable, as indicated earlier, to have present a small proportion of a pigment-suspending agent as castor wax or a polyvalent metal stearate such as, e.g., zinc stearate, cadmium stearate, or aluminum stearate, to prevent the settling of ingredient (A), the zinc dust, from the other ingredients of the coating composition. In most instances it is also desirable to dilute one or more of the characterizing ingredients or mixtures of two or more such ingredients with a viscosity-reducing amount of a volatile solvent so as to facilitate the application of the coating composition to metal surfaces. Solvents useful for this purpose include those which are commonly employed in the paint and lacquer industries such as, for example, petroleum hydrocarbon solvents such as, petroleum aromatic spirits; alcohols such as, e.g., methyl, ethyl, propyl, butyl, and amyl alcohols; ketones such as, e.g., acetone, diethyl ketone, methyl isobutyl ketone, methyl ethyl ketone, etc.; the lower chlorinated alkanes such as, e.g., ethylene dichloride, 1,2-dichloropropane, butyl chloride, etc.; aromatic hydrocarbons such as, e.g., benzene, toluene, xylene, mesitylene, etc.; and aliphatic ethers such as, e.g., diisopropyl ether, diisobutyl ether, and the like. In certain instances it is desirable to use mixtures of 2 or more solvents. The aromatic petroleum spirits useful in adjusting the viscosity of the compositions of the present invention are available from various petroleum refiners. These petroleum-derived solvents generally boil in the range from about 300-400° F. and have a Kauri-butanol value from about 50 to about 125. An economical, commercially available mixture of aromatic petroleum spirits boils in the range 316-349° F. and has a Kauri-butanol value of about 91.

Although the proportions of the several ingredients are not particularly critical, best results from the standpoint of economy, ease of application, and weldability of the coated metal surface are obtained when one uses a composition prepared from the mixture of from about 300 to about 450 parts, preferably from about 350 to about 400 parts, of ingredient (A), the zinc dust; from about 5 to about 70 parts, preferably from about 10 to about 40 parts, of ingredient (B), the metal-containing organic phosphate complex; and from about 6 to about 80 parts, preferably from about 12 to about 60 parts, of ingredient (C), the metal-free organic phosphate complex. To this mixture there may be added, optionally, a small amount, generally from about 1 to about 10 parts, more often from about 2 to about 6 parts, of a pigment-suspending agent and at least about 10 parts, preferably from about 15 to about 120 parts, of a viscosity-reducing solvent. The use of a pigment-suspending agent, although not absolute-

ly essential, is required if settling of the zinc dust is to be avoided. In the absence of this agent, the composition must be stirred at frequent intervals after preparation and during use. Thus, for obvious practical reasons it is highly desirable to include a pigment-suspending agent in the compositions of this invention.

The order of mixing the ingredients of the composition is not particularly critical. It is generally most convenient, however, to mill the pigment-suspending agent, is used, in all or a portion of the solvent-diluted ingredient (B), the metal-containing organic phosphate complex, by means of a ball mill or other conventional paint-dispersing equipment. This mixture is then removed to another vessel equipped with means for vigorous stirring and ingredient (A), the powdered zinc, and the balance, if any, of ingredient (B) are added and stirred well. A small proportion of solvent, either added directly to the vessel contents or present in ingredient (B) serves to facilitate the mixing operation. After the mixture has been stirred for a sufficient time to become homogeneous, ingredient (C), the metal-free organic phosphate complex, is added while the whole is stirred vigorously. The consistency of the mass is then adjusted by the addition, if desired, of a further amount of solvent so as to yield a composition which has a viscosity well-suited for the particular method by which it is to be applied to a metal surface. The application to a metal surface may be made by any one of the methods commonly used in the paint industry such as dipping, brushing, roller-coating, flow-coating, or spraying.

Although any of the various ingredients (A) through (C) described earlier may be used in compounding the compositions of the present invention, certain ingredients and combinations thereof are preferred for reasons of their commercial availability and economy. Thus, for example, a very useful and economical group of compositions of this invention contain as essential ingredients:

(A) From about 300 to about 450 parts, preferably from about 350 to about 400 parts, of powdered zinc;
(B) From about 5 to about 70 parts, preferably from about 10 to about 40 parts, of a zinc-containing organic phosphate complex prepared by the process which comprises the reaction of

(I) A zinc salt of the acid phosphate esters derived from the reaction of a phosphorus-containing reagent selected from the group consisting of phosphorus pentasulfide and phosphorus pentoxide with a mixture of a monohydric alcohol and from 0.25 to 4.0 equivalents of a polyhydric alcohol, and
(II) At least about 0.1 equivalent of an aliphatic epoxide;

(C) From about 6 to about 80 parts, preferably from about 12 to about 60 parts, of a metal-free organic phosphate complex prepared by the process which comprises mixing 1 mole of phosphorus pentoxide, from about 0.2 to about 12.5 moles of a copolymer of allyl alcohol and styrene having an average molecular weight within the range from about 750 to about 1500, from about 0.3 to about 5.0 moles of a mono-alkyl phenol containing at least about 5 carbon atoms in the alkyl group, and heating said mixture at a temperature within the range from about 75° to about 150° C.;

(D) At least about 10 parts, preferably from about 15 to about 120 parts, of a volatile solvent selected from the group consisting of petroleum hydrocarbon solvents, alcohols, ketones, lower chlorinated alkanes, aromatic hydrocarbons, and aliphatic ethers and, optionally,

(E) From about 1 to about 10 parts, preferably from about 2 to about 6 parts, of castor wax.

Specific illustrations of the preparation of compositions of this invention are as follows. All parts are by weight unless otherwise indicated.

EXAMPLE I

4.0 parts of a commercial grade of castor wax known as "Thixcin R" is dispersed in 10 parts of the product of

Example B-3 and 18 parts of "Solvent X" (petroleum aromatic spirits boiling in the range 316-349° F. and having a kauri-butanol value of 91). After the castor wax is thoroughly dispersed (15 minutes is normally required when a conventional paint shaking machine is used), the whole is transferred to a vessel equipped with a propeller-type stirring device and 44 parts more of the product of Example B-3 and 375 parts of powdered zinc passing 325-mesh screen are added. The ingredients are stirred vigorously until they form a homogeneous mass. Thereafter, 18.75 parts of the product of Example C-2 and 10 parts of Solvent X are added to the contents of the vessel and the whole is stirred until all of the ingredients are uniformly mixed together. The composition is then ready for packaging or use.

In a manner like that described in Example I, a number of fluid compositions of the invention are prepared using the ingredients and proportions thereof shown in Table 4. The two-fold additions of the metal-containing organic phosphate complex and the solvent (if any) are made using the same relative proportions observed in Example I.

Table 4

Example No.	Zinc Powder,* parts	Metal-containing organic phosphate complex		Metal-free organic phosphate complex		Pigment-suspending agent		Solvent added	
		Product of Ex. No.	Parts	Product of Ex. No.	Parts	Identity	Parts	Identity	Parts
II.....	375	B-3.....	17.5	C-2.....	31.4	Thixcin R.....	3.7	Solvent X.....	35.9
III.....	440	B-3.....	43.1	C-2.....	46.2	do.....	4.5	do.....	31.5
IV.....	440	B-3.....	21.5	C-2.....	69.3	do.....	4.5	do.....	46.5
V.....	375	B-3.....	35.9	C-2.....	19.2	do.....	4	do.....	37
		B-4.....	22.6						
VI.....	375	B-3.....	17.9	C-2.....	38.5	do.....	4	do.....	36
		B-4.....	22.6						
VII.....	375	B-2.....	28.7	C-2.....	39.7	do.....	3.8	Toluene.....	9
VIII.....	375	B-2.....	28.7	C-2.....	39.7	do.....	3.8	Solvent X.....	21.9
IX.....	375	B-2.....	14.3	C-2.....	59.5	do.....	3.8	None used.....	
X.....	375	B-2.....	14.3	C-2.....	59.5	do.....	3.8	Toluene.....	34.8
								None used.....	
XI.....	375	B-2.....	30	C-2.....	69.3	do.....	3.8	Toluene.....	23.8
XII.....	375	B-2.....	30	C-2.....	69.3	do.....	3.8	Solvent X.....	9
								None used.....	
XIII.....	375	B-2.....	15	C-2.....	90	do.....	3.8	Toluene.....	27
XIV.....	375	B-2.....	15	C-2.....	90	do.....	3.8	Solvent X.....	22.5
XV.....	375	B-2.....	42	C-2.....	61.2	do.....	3.8	None used.....	
							7.9	Toluene.....	42.3
								Solvent X.....	21.2
XVI.....	375	B-2.....	52	C-2.....	22.7	do.....	8.1	Solvent X.....	20.7
				C-1.....	71.4				
XVII.....	310	2 of U.S. 2,820,723.	65	C-3.....	9	Zinc stearate.....	2	Ethylene dichloride.....	25
XVIII.....	340	4 of U.S. 2,820,723.	5.5	C-6.....	15	Cadmium stearate.....	9	Xylene.....	20
XIX.....	410	2 of Ser. No. 139,845.	23	C-7.....	25	Aluminum stearate.....	7	Methylisobutyl.....	30
								Mesitylene.....	42
XX.....	360	7 of Ser. No. 139,845.	20	C-8.....	40	Thixcin R.....	1.5	Diisopropyl ether.....	10
								Cumene.....	30

*Passing 325-mesh screen.

The compositions of this invention are generally applied to the metal surface to be protected in an amount sufficient to yield a dried film thickness of from about 0.5 to about 10 mils and preferably from about 1 to about 3 mils. After application to the metal surface, the composition may be dried by any one of the various methods commonly employed in the paint and lacquer industry such as air-drying at ambient temperature, drying in a current of hot air, baking in an oven, or baking under a bank of infra-red lamps. In general, best results from the standpoint of good adherence and corrosion protection are obtained with the compositions of this invention when a film thereof is air-dried at ambient temperature. Oven-baking procedures, which are useful in some instances, however, call for exposure of the coated metal surface to temperatures in the range of 250-450° F. for a period ranging from about 1 minute to about 1 hour. The lower baking temperatures generally require longer periods of time than the higher baking temperatures; for example, typical procedures call for baking at 400° F. for 2 minutes, or 15 minutes at 360° F., or 45 minutes at 250° F.

In most instances the compositions of this invention

will be applied directly to the bare metal surface to be protected. In certain applications however, where superior corrosion resistance is sought, the metal may be pretreated with a metal passivating solution such as, e.g., a dilute chromic acid solution, or an aqueous phosphating solution such as, e.g., aqueous acidic zinc dihydrogen phosphate, aqueous acidic manganese dihydrogen phosphate, and the like. Such metal passivating or phosphating techniques are well-known and are described, for example, in U.S. Patents 1,206,075; 1,247,668; 1,305,331; 7,485,025; 1,610,362; 1,980,518; 2,001,754; 2,901,385; 2,846,342; 2,868,682; 2,901,437; and 2,876,150. A very useful and effective class of aqueous phosphating solutions containing as essential ingredients zinc ion, phosphate ion, nitrate ion, and calcium ion are described in U.S. application Ser. No. 373,449, filed August 5, 1953.

In addition to the pretreatment of the metal surface, it may also be desirable in certain instances, particularly where decorative effects are sought, to "top-coat" the dried film of a composition of this invention with a paint, paint primer, lacquer, or enamel. The compositions of this invention serve as an excellent base for such top-

coats in that they inhibit the deterioration of the underlying base metal and thereby remove the principal cause of blistering, flaking, and other forms of loss of coating adhesion. The above discussion regarding pretreatment of the metal surface and top-coating of the dried film of the compositions of this invention is not to be construed as indicating that such pretreatments or post-treatments are at all required for adequate protection of metal surfaces. It has been offered merely to point out the versatility of the present compositions in adhering well to modified metal surfaces and in providing an excellent paint base in applications where a top-coat must be applied.

Tests were carried out to determine the efficacy of the present compositions in retarding corrosion of ferrous metal surfaces. In all of the tests, 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 used to receive films of the coating compositions of this invention. The compositions were brushed on the steel panel and dried in the indicated manner to provide a film having a thickness of 1.5±0.2 mils.

The prepared panels were then subjected to a salt fog corrosion test.

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% aqueous sodium chloride is maintained in contact with the test panels for a predetermined time at $95^{\circ} \pm 2^{\circ}$ F.

In the 120-hour test, the coating on the panel is pierced with a pointed instrument to yield a vertical scribe beginning one inch from the top of the panel and ending one inch from the bottom thereof. The panel is then placed in the salt fog chamber for 120 hours and removed for inspection. The "creep" rating is the average loss of coating from each side of the scribe expressed as an integer which represents the number of thirty-seconds of an inch. The panel is also visually inspected for rust and the amount thereof is reported as "percent of area rusted."

In the 250-hour test, duplicate unscribed, coated panels are placed in the salt fog chamber for 250 hours and then removed for inspection. The amount of rust on each panel is noted and the average for the two panels is reported as "average per cent of area rusted." An unprotected steel panel becomes rusted over its entire surface (i.e., fails) in one hour or less when subjected to this test.

Although no specific test standards have yet been promulgated by industry, past experience indicates that a composition which holds corrosion to a value not greater than about 15 percent in the 250-hour test and, optionally, has a creep rating not greater than about 4 will perform satisfactorily in the field.

The test results obtained on a number of compositions of this invention are set forth in Table 5.

Table 5

Composition of Ex. No.	Salt fog corrosion test results			
	Panel preparation ¹	Test, hours	Creep rating	Average percent of area rusted ²
I.....	A.....	250	-----	0.5
	B.....	250	-----	0.5
III.....	A.....	250	-----	10
	B.....	250	-----	6
IV.....	A.....	250	-----	3.5
	B.....	250	-----	12.5
V.....	A.....	250	-----	3
VI.....	A.....	250	-----	3.5
	B.....	250	-----	15
VII.....	A.....	250	-----	1
	A.....	120	1	1
VIII.....	A ³	250	-----	3
	A ³	120	1.5	0
IX.....	A.....	250	-----	12.5
	A.....	120	0	1
XI.....	A.....	250	-----	2
	A.....	120	1.5	1
XIII.....	A.....	250	-----	9
	A.....	120	0	1
XV.....	A.....	250	-----	2
	B.....	120	1.5	2
XVI.....	A.....	250	-----	1
	A.....	120	1	0
	B.....	120	1	2

¹ A=air-dried at ambient temperature. B=baked 15 minutes at 360° F.

² A minus sign (-) after a value denotes that the percent of area rusted is somewhat less than the given value would indicate. The inspection for rust does not include the so-called "white corrosion" which results from the conversion of the zinc powder to zinc salts and which is expected in zinc-filled paints that protect ferrous surfaces by the sacrificial consumption of zinc metal.

³ These panels were coated by means of a sprayer.

In addition to their utility as protective coating materials for ferrous metals, the compositions of this invention are also useful in protecting non-ferrous metals and alloys thereof such as aluminum, magnesium, magnesium, copper, brass, bronze, white metal, Dowmetal, etc., against corrosion. They are also useful as protective coating materials on galvanized ferrous surfaces, on plated metal surfaces such as, e.g., copper-plated, nickel-plated, and cadmium-plated ferrous surfaces, and on phosphated metal surfaces. 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 Serial No. 373,449, filed August 10, 1953, now Patent No. 3,090,709. It is intended that the entire disclosure of Serial No. 373,449, now Patent No. 3,090,709, be incorporated herein by reference.

What is claimed is:

1. A fluid composition adapted to form a protective coating on metals which contains as essential ingredients:

(A) from about 300 to about 450 parts of finely divided zinc,

(B) from about 5 to about 70 parts of a metal-containing organic phosphate complex prepared by the process which comprises the reaction of

(I) a polyvalent metal salt of the acid phosphate esters derived from the reaction of a phosphorus-containing reagent selected from the group consisting of phosphorus pentasulfide and phosphorus pentoxide with a mixture of monohydric and polyhydric alcohols, and

(II) at least about 0.1 equivalent of an organic epoxide having from 2 to about 57 carbon atoms, and

(C) from about 6 to about 80 parts of a metal-free organic phosphate complex prepared by the process which comprises mixing one mole of phosphorus pentoxide, from about 0.2 to about 12.5 moles of a copolymer of allyl alcohol and a styrene, and from about 0.3 to about 5.0 moles of an alkylphenol, and heating said mixture at a temperature within the range from about 75° C. to about 150° C.

2. A composition in accordance with claim 1 further characterized in that ingredient (C) has been acylated with a high molecular weight carboxylic acid compound selected from the group consisting of unsaturated aliphatic carboxylic acids containing at least 12 carbon atoms and esters thereof.

3. A composition in accordance with claim 1 further characterized in that it additionally contains a pigment-suspending agent selected from the group consisting of castor wax and polyvalent metal stearates.

4. A composition in accordance with claim 1 further characterized in that the polyvalent metal salt of (B)-I is a zinc salt.

5. A composition in accordance with claim 1 further characterized in that the alkylphenol of (C) is a monoalkyl phenol.

6. A fluid composition adapted to form a protective coating on metals which contains as essential ingredients:

(A) from about 300 to about 450 parts of powdered zinc,

(B) from about 5 to about 70 parts of a zinc-containing organic phosphate complex prepared by the process which comprises the reaction of

(I) a zinc salt of the acid phosphate esters derived from the reaction of a phosphorus-containing reagent selected from the group consisting of phosphorus pentosulfide and phosphorus pentoxide with a mixture of monohydric alcohol and from 0.25 to 4.0 equivalents of a polyhydric alcohol, and

(II) at least about 0.1 equivalent of an aliphatic epoxide having from 2 to about 57 carbon atoms,

(C) from about 6 to about 80 parts of a metal-free organic phosphate complex prepared by the process which comprises mixing one mole of phosphorus pentoxide, from about 0.2 to about 12.5 moles of a

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copolymer of allyl alcohol and styrene having an average molecular weight within the range of from about 750 to about 1500, from about 0.3 to about 5.0 moles of a mono-alkyl phenol containing at least about 4 carbon atoms in the alkyl group, and heating said mixture at a temperature within the range of from about 75° C. to about 150° C., and

(D) at least about 10 parts of a volatile solvent selected from the group consisting of petroleum hydrocarbon solvents, alcohols, ketones, lower chlorinated alkanes, aromatic hydrocarbons, and aliphatic ethers.

7. A composition in accordance with claim 6 further characterized in that it additionally contains from about 1 to about 10 parts of castor wax.

8. A composition in accordance with claim 6 further characterized in that the powdered zinc of (A) passes 325-mesh screen.

9. A composition in accordance with claim 6 further characterized in that the zinc salt of (B)-I is the zinc salt of the acid phosphate esters derived from the reaction of a phosphorus-containing reagent selected from the group consisting of phosphorus pentasulfide and phosphorus pentoxide with a mixture of about equivalent amounts of isooctyl alcohol and dipropylene glycol.

10. A composition in accordance with claim 6 further

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characterized in that the aliphatic epoxide of (B)-II is butyl epoxystearate.

11. A composition in accordance with claim 6 further characterized in that the aliphatic epoxide of (B)-II is beta-propiolactone.

12. A method of inhibiting the corrosion of a metal surface which comprises applying thereto a film of the fluid composition of claim 1.

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

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