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COMPOSITIONS AND METHODS FOR FORMING COATINGS ON METAL SURFACES

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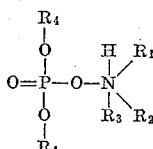
This invention relates to a method of and compositions for forming protective coatings on metal surfaces which are susceptible to atmospheric corrosion. More particularly this invention relates to compositions and a film-forming constituent in an aqueous alkaline media.

In the preparation of metal surfaces for receiving organic film coatings such as paint, varnish, lacquers and the like, it is now conventional to preliminarily condition the surface by applying thereto a protective phosphate coating which serves to improve the corrosion resistance and to bind the subsequently applied organic film-forming materials to the metal surface. Such a procedure ordinarily involves the separate steps of preliminarily cleaning the metal, subjecting it to aqueous acidic solutions which deposit an integrally bound phosphate coating on the surface, rinsing and thereafter applying the paint, lacquer or the varnish or the like.

In accordance with this invention it has now been found that the preliminary step of separately forming a phosphate coating on a metal surface can be eliminated by combining certain amine phosphate compounds with certain types of compatible organic film-forming resins which are either water soluble or water dispersible. The improved compositions of this invention are dispersions which have a pH in the range of about 7 to about 11, the dispersing media being primarily water but may include water miscible or water-compatible organic solvents.

In general, the improved compositions of this invention may be applied to the surfaces of any of the commercial metals which are susceptible to atmospheric corrosion including steel, iron, zinc, aluminum, cadmium, magnesium, copper bearing materials including the alloys thereof and the like. The coatings are formed by applying the compositions of this invention to the surface, at room temperature, by spraying, brushing, rolling or the like and thereafter raising the temperature of the coated metal surface to a temperature sufficient to expel, vaporize or otherwise remove the dispersing media, to induce reaction between the surface and the phosphate constituent of the composition and to effect a cure of the resinous components of the composition to thus form a tightly bound adherent and integral, impervious coating on the metal surface.

The phosphates which are suitable for the purposes of this invention are the amine phosphates, substituted amine phosphates, and the ammonia and amine reaction products of zinc or manganese phosphates. More specifically, the satisfactory amine phosphates are those phosphates which have the following structure:



wherein R_1 and R_2 may each be a member of a class consisting of hydrogen and hydrocarbon radicals having 1 to 12 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl, R_3 is a member of the class consisting of hydrogen and hydrocarbon radicals having 1 to 20 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl; R_4 is a member of a class consisting of

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H, NH_2 , and hydrocarbon radicals having 1 to 20 carbon atoms, and wherein the foregoing hydrocarbon radicals may contain hydroxyl, bromo, chloro-, sulfo-, nitro-, and amino substituent groups.

It has also been found that the above type of amine phosphate may be replaced satisfactorily by an amine phosphate of the heterocyclic amine type such as pyridine and morpholine phosphate, or pyridine or morpholine phosphates which are ring substituted with a hydrocarbon radical having 1 to 20 carbon atoms, and of the group consisting of alkyl, aryl and cycloalkyl radicals. Preferred amine phosphates for the purposes of this invention are the alkyl amine phosphates having 2 to 6 carbon atoms, the diamine phosphates such as the ethylenediamine phosphates and pyridine phosphate. Of the alkyl amine phosphates, butylamine phosphate has been found to give the best results.

The amine or alkyl ammonium phosphates may be added to the aqueous resin containing compositions as such or in the form of aqueous solutions or they may be in the form of a dispersion where the amine is one containing the higher carbon chain length substituents. Such amine phosphates are conveniently formed by reacting the selected amine and phosphoric acid, zinc or manganese phosphate in water to produce the desired amine phosphate. It will be appreciated that the PO_4 content of the amine phosphates may be varied, but the amount of amine which is present should be sufficient to form an amine phosphate aqueous solution or dispersion having a pH in the range of about 7 to about 11. The phosphate content of the compositions of this invention is derived solely from the amine phosphate and since it becomes diluted when admixed with the aqueous resin component, an H_3PO_4 equivalency of 10 or above in the selected amine phosphate is normally desirable. The expression " H_3PO_4 equivalency" as used herein and in the appended claims refers to the weight in grams of H_3PO_4 in 100 ml. of the amine phosphate solution, and for ease in identification the H_3PO_4 equivalency will be indicated by the number following the designation "BAP," for example, BAP-10 refers to butyl amine phosphate having an H_3PO_4 equivalency of 10.

As stated above, the phosphate of this invention includes the reaction product of reacting zinc phosphate with ammonia or with an amine of the above specified type. For this purpose the zinc phosphate may be a primary zinc phosphate, a monohydrogen or a dihydrogen zinc phosphate. The zinc-amino complex reaction product is believed to be a zinc or manganese coordination compound and may be formed, for example, by adding ammonium hydroxide to an aqueous slurry containing approximately equal parts of tertiary zinc phosphate and zinc oxide or tertiary zinc phosphate and zinc carbonate. Such zinc-amino complex reaction products should contain a ratio of zinc to PO_4 of less than 16.6 to 1 and preferably less than 6 to 1 with the best results being obtained from compositions having a zinc to PO_4 ratio of about 3 to 1.

In accordance with this invention it has been surprisingly found that the above described amines form compatible and stable aqueous dispersion with a wide variety of water dispersible or water soluble resins so long as the dispersion is maintained at a pH within the range of about 7 to about 11. In the event the pH is below about 7, difficulty is encountered with many of the water dispersible resin systems such as by flocculation, curdling or the like. In order to form compositions having a pH which exceeds about 11 it is necessary to add a substantial quantity of a strong alkali, such as sodium hydroxide, and this is undesirable because it forms water-soluble constituents in the resulting coating which are detrimental.

The amine phosphate should be present in the composition in an amount sufficient to provide an H_3PO_4 equiva-

lency in the range of about 0.05 to about 10 and a preferred concentration is in the range which will give an H_3PO_4 equivalency between about 3 and about 8.

Throughout this specification and the appended claims, figures given in percent refer to percent w./v., that is, percent by weight per unit of volume of the solution.

The water dispersible or water soluble resins which are suitable for the purposes of this invention are those resins which form films upon heating at temperatures sufficient to expel or drive off the dispersing medium or to cause thermosetting thereof, at temperatures of about 300° F.-450° F., and which film is continuous, adherent and impervious to corrosive media such as moisture, saline solutions and the like. The resins must be capable of being formed into stable solutions, dispersions, or emulsions and must remain stable over a pH range of about 7 to about 11. A large number of specific resins and a variety of chemical types of resins have been found to form such stable, useful dispersions, emulsions or solutions with the above specified amine phosphates, although the same resins do not function satisfactorily with other known phosphates. These resins comprise the polyvinyl acetate resins, the alkyd resins, the acrylic resins, the epoxy resins, the polyvinyl butyral resins, the polyvinylidene chloride resins, and the copolymers of polyvinyl pyrrolidone and styrene, or polyvinyl pyrrolidone and ethyl acrylate. Of the water dispersible resins set forth above, the alkyds constitute the preferred type of resins for the purposes of this invention. Water soluble phenolic resins are also suitable, and particularly suitable are the diphenolic acid-amine adducts which have been modified with formaldehyde, such as the resins available under the commercial designation of S. C. Johnson & Son, Inc., as SRE-1134.

The alkyd resins which are suitable for the purposes of this invention include those polyesters which are modified with oxidizing or non-oxidizing fatty acids which may be derived from either vegetable or mineral oils. The alkyds may be of the short oil, medium oil or long oil modified types and the oil may be, for example, soya bean, dehydrated castor oil, cotton seed oil, or the like. The oil modified alkyds may be further modified with rosin, phenolic resin, styrenes, acrylics or epoxy resins which produce copolymers. The preferred type of alkyd resin is one manufactured from phthalic anhydride and a polyhydric alcohol, such as glycerol, or pentaerythritol or the like, by the use of conventional manufacturing procedures. The non-phthalic alkyds are also useful, however, that is, alkyds made from the preliminary reaction between a rosin or turpene and maleic anhydride or fumaric acid which is then esterified with glycerol or a fatty acid glyceride. It is also satisfactory to modify the alkyds with polyamides.

Specific examples of alkyd resins of the above described type which are suitable for the purposes of this invention are the oil modified isophthalic alkyds, commercially designated Cargill #1302 available from Cargill, Inc., and the rosin oil modified alkyd emulsion, commercially designated Synthemul 1505, and the drying oil modified alkyd emulsion, commercially designated Synthemul 1506, and available from Reichhold Chemical Company.

In the acrylic resin class, the acrylic esters are particularly satisfactory and specifically ethyl acrylates, methyl acrylates, methoxy ethyl acrylates, ethoxy ethyl acrylates, 2-diethyl-amino ethyl, t-butyl amino ethyl methacrylates perform satisfactorily.

In the class of vinyl resins, satisfactory compositions have been prepared including polyvinyl butyral, polyvinylidene chloride and copolymers of polyvinyl pyrrolidone and ethyl acrylate. The polyvinyl acetate resins which are preferred are the soft copolymers which do not require external plasticization, particularly the copolymers including as the co-monomer ethyl acrylate, or dibutyl

fumarate, but it is also satisfactory to employ polyvinyl acetate homopolymer emulsions.

The epoxy resins which are suitable may be any of the low melting point glycidyl polyethers which are liquid at room temperature, such as, for example, the reaction products of 1 to 2 or more moles of epichlorohydrin and a dihydric phenol such as Bisphenol A, in the presence of the base such as sodium hydroxide. The epoxy resins may be either the type which is cured with amines or may be the type which is modified so as to form esters capable of being air dried or baked. The ester type of epoxy resin is satisfactorily emulsified and combined with an alkyl amine phosphate such as butylamine or isopropylamine phosphate to form a highly satisfactory composition for purposes of this invention. Epoxies which are based on butadiene or epoxidized oils are also satisfactory for the purposes of this invention. A preferred form of this invention constitutes the concurrent presence in the composition of a diamine and a liquid epoxy resin of the unmodified type above specified. In this event, upon heating of the composition on the surface the diamine phosphate releases diamine which serves to cure the epoxy resin in situ on the surface.

The compositions of this invention may also contain wetting agents, preferably wetting agents of the type which evaporate at temperatures in the range of 300-450° F., for example, 3,5 dimethyl-1 hexyn-3-ol, commercially available under the designation Surfynol 61 from Air Reduction Chemical, having a boiling point of about 150° C. The preferred compositions also include a pigment such as titanium dioxide, iron oxide, chromium oxide, viscosity modifiers such as bentonite, kaolin, silica aerogel or the like. Such pigments are also to be understood to include conventional driers or polymerization catalysts for the resin in the composition but such modifiers as these are present in only minor quantities. The pigment, however, may be present in an amount as high as about 50%, w./v. Compositions having a percent pigment volume, that is, the ratio of the pigment volume to the volume of pigment plus the resin solids, expressed as percent, in the range of about 25% to about 45% are particularly suitable for automobile finishing and the like.

In compositions which do not include any pigment, the resin solids may constitute as high as about 40% w./v., of the composition. In pigment compositions, however, the resin concentration is preferably in the range of about 1 to about 20%. The most preferred compositions include 5-15% resin, have an H_3PO_4 equivalency in the range of 3-8 and have a percent pigment volume concentration in the range of 25% to about 45%.

The following examples illustrate the compositions and method of this invention in greater detail but it is to be understood that the specific materials and conditions employed therein are illustrative of this invention only and do not define its limits which have been hereinabove set forth.

EXAMPLE I

An n-butylamine phosphate aqueous solution was prepared by slowly adding n-butylamine to a 2,000 ml. quantity of a 50% aqueous H_3PO_4 solution, with stirring, until a total quantity of 1,178 grams of the n-butylamine had been added. The solution was stirred until it was uniformly blended and was found to have a pH of 7.0-7.1. A master batch of butylamine phosphate was formed by adding sufficient water to the composition to form a material having an H_3PO_4 equivalency of 25. A portion of this master batch was then diluted with additional water to form a butylamine phosphate aqueous solution having an H_3PO_4 equivalency of 10.

A number of different aqueous resin dispersions and solutions were then mixed with separate portions of the butylamine phosphate solution to form compositions for application to metal surfaces to form protective coatings.

In each case the resin dispersion was first diluted with water and then the butylamine phosphate solution was stirred into the diluted resin dispersion until a uniform blend was obtained and thereafter additional water was added to the blended composition to form a final composition

Table I

Resin Dispersion or Solution	Wt. Used Parts	Water Parts	BAP-10 Parts	Total	Comments
1. Polyvinyl Acetate Copolymer Emulsion	7.3	7	4	20	Uniform Emulsion.
Control	7.3	7	0	20	Do.
2. Oil Modified Isophthalic Alkyd Emulsion	6.7	8	4	20	Uniform Emulsion.
Control	6.7	8	0	20	Do.
3. Polyvinyl Acetate Copolymer Emulsion	7.7	7	4	20	Uniform Emulsion.
Control	7.7	7	0	20	Do.
4. Polyvinyl Acetate Copolymer Emulsion	8.0	7	4	20	Uniform Emulsion.
Control	8.0	7	0	20	Do.
5. Diphenolic Acid-Triethanolamine Ester-Formaldehyde Condensation Product	9.3	5	4	20	Uniform Emulsion.
Control	9.3	5	0	20	Do.
6. Polyvinyl Acetate Copolymer Emulsions	7.3	7	4	20	Uniform Emulsion.
Control	7.3	7	0	20	Do.
7. Polyvinyl Acetate Copolymer Emulsions	7.3	7	4	20	Uniform Emulsion.
Control	7.3	7	0	20	Do.
8. Polyvinyl Pyrrolidone Ethyl Acrylate Copolymer	10.0	5	4	20	Uniform Emulsion.
Control	10.0	5	0	20	Do.
9. Polyvinyl Pyrrolidone Styrene Copolymer	10.0	5	4	20	Uniform Emulsion.
Control	10.0	5	0	20	Do.
10. Non-Ionic Acrylic Polymer Emulsion	8.9	6	4	20	Uniform Emulsion.
Control	8.9	6	0	20	Do.
11. Rosin Modified Alkyd Emulsion	8.9	6	4	20	Uniform Emulsion.
Control	8.9	6	0	20	Do.
12. Drying Oil Type Alkyd Emulsion	8.0	7	4	20	Uniform Emulsion.
Control	8.0	7	0	20	Do.
13. Acrylic Copolymer	8.0	7	4	20	Uniform Emulsion.
Control	8.0	7	0	20	Do.
14. Polyvinyl Acetate Emulsion	7.3	7	4	20	Uniform Emulsion.
Control	7.3	7	0	20	Do.
15. Polyvinyl Acetate Emulsion	8.0	7	4	20	Uniform Emulsion.
Control	8.0	7	0	20	Do.

1. CI-202—Celanese Corp.
2. C-1302—Cargill Inc.
3. Flexbond 800—Air Reduction Chemical & Carbide Co.
4. Flexbond F-186—Air Reduction Chemical & Carbide Co.
5. Johnson's Water Soluble SR E-1134—S. C. Johnson & Son Inc.
6. Polyco 804—Borden Chemical Co.
7. Polyco 806—Borden Chemical Co.
8. Polectron 130—Gen. Aniline & Film Co.
9. Polectron 430—Gen. Aniline & Film Co.
10. Rhoplex C-72—Rohm & Haas Co.
11. Synthemul 1505—Reichhold Chemicals, Inc.
12. Synthemul 1506—Reichhold Chemicals, Inc.
13. UBATOL 7001—UBS Chemical Co.
14. WALLPOL 9120—Reichhold Chemicals, Inc.
15. WC 130—Union Carbide Plastics Co.

containing 20% resin solids and having a 2% H_3PO_4 equivalency. The specific quantities of resin dispersion, amount of water added to dilute that dispersion, the amount of butylamine phosphate solution added and the total quantity of solution, for each case, are set forth in tabular form in Table I. For each resin-butylamine phosphate composition a control was prepared containing an identical quantity of resin solids in water but free of butylamine phosphate, which control was used for visual comparison of the appearance of the resulting dispersion or emulsion.

EXAMPLE II

Each of the compositions identified in Example I as compositions 1-15 inclusive were used to form coatings on cold rolled steel panel surfaces. The panels were preliminarily conventionally cleaned by vapor degreasing and wiping and then a plurality of panels were immersed in each of the compositions designated 1-15 of Example I, removed, air dried for 30-60 minutes and thereafter baked at 375° F. for 15 minutes.

Similarly cleaned panels were immersed in the control aqueous resin dispersions corresponding to each of the compositions numbered 1-15 of Example I, removed, air dried for 30-60 minutes and baked for 50 minutes at 375° F. After cooling, a portion of the coated surface on the panels produced from compositions 1-15, and from the control solutions corresponding to compositions 1-15, were contacted with an organic solvent, in most cases

methyl isobutyl ketone. In each case the resin coating was dissolved and an inspection was made of the surface beneath the portion of the coating which was dissolved. The appearance of each of the surface portions is described in tabular form in Table II.

Table II

Resin Dispersion or Solution	Comments
50 1. Polyvinyl Acetate Copolymer Emulsion	Bluish, Iridescent.
Control	Colorless.
2. Oil Modified Isophthalic Alkyd Emulsion	Bluish.
Control	Colorless.
3. Polyvinyl Acetate Copolymer Emulsion	Bluish, Iridescent.
Control	Colorless.
4. Polyvinyl Acetate Copolymer Emulsion	Bluish, Gray and Tan.
Control	Stain (Slight).
5. Diphenolic Acid-Triethanolamine Ester-Formaldehyde Condensation Product	Red-Blue Iridescent.
Control	Colorless.
6. Polyvinyl Acetate Copolymer Emulsions	Bluish, Iridescent and Gold.
Control	Rusty Stain.
60 7. Polyvinyl Acetate Copolymer Emulsions	Bluish, Iridescent.
Control	Tan Stain.
8. Polyvinyl Pyrrolidone Ethyl Acrylate	Sl. Bluish.
Control	Colorless.
9. Polyvinyl Pyrrolidone Styrene	Sl. Bluish.
Control	Colorless.
10. Non-Ionic Acrylic Polymer Emulsion	Bluish-Iridescent.
Control	Colorless.
65 11. Rosin Modified Alkyd Emulsion	Bluish.
Control	Colorless.
12. Drying Oil Type Alkyd Emulsion	Bluish.
Control	Colorless.
13. Acrylic Copolymer	Bluish, Iridescent.
Control	Colorless.
14. Polyvinyl Acetate Emulsion	Bluish, Iridescent.
Control	Colorless.
70 15. Polyvinyl Acetate Emulsion	Bluish.
Control	Tan Amber Stain.

The following example illustrates the effect of variation of the phosphate concentration on the compatibility of the resin component in the composition.

EXAMPLE III

The composition was prepared using the same resin as the resin used in composition 1 of Example I and to 7.3 parts of that resin dispersion 4 parts of water was added and blended to uniformity. To this blend 8 parts of butylamine phosphate having a PO_4 equivalency of 10 was added, the total brought to 20 parts with water, and the resulting dispersion was observed to retain the appearance of the control. To 7.3 parts of the same but undiluted resinous dispersion, 12 parts of BAP-10 was added, the total adjusted to 20 parts with water and at this concentration slight agglomeration of the particles was noticeable, but the emulsion thereafter remained stable.

A composition was prepared by adding to 8.9 parts of Synthemul #1505, 4 parts of water and thereafter 8 parts of BAP-10 with adjustment with water to a total of 20. A stable uniform emulsion was obtained. Another sample was prepared by adding 12 parts of BAP-10 to 8.9 parts of Synthemul #1505 dispersion and a uniform emulsion having the appearance of the control was formed. To another 8.9 parts of the Synthemul #1505 resin 5.3 parts of BAP 30 was added and the total adjusted to 20 parts with water and at this concentration, which corresponds to an H_3PO_4 equivalency of 8, the initiation of particle agglomeration was detected, although the emulsion was stable thereafter.

EXAMPLE IV

A batch of diethylenetriamine phosphate was prepared by using the procedures described above in Example I to form butylamine phosphate except that when a sufficient quantity of the diethylenetriamine phosphate had been added to produce a pH of 7.0 the addition was stopped, the composition was concentrated over a steam bath and then was completely dried in an oven at 250° F. The dried product was then powdered.

3 parts of the powered diethylene triamine phosphate was admixed with 100 parts of water, 1 part of hydroxy ethyl cellulose, as Cellosize QP 4400, and 20 parts of an unmodified liquid epoxy resin. Sufficient ammonium hydroxide was added to adjust the pH to 7 and the resulting dispersion was uniform and free of agglomerates. The epoxy resin was the material commercially designated Epi-Rez #2051, Jones-Dabney Company.

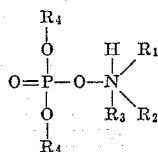
Another composition was prepared by admixing 4.5 parts of the diethylenetriamine phosphate described above, 60 parts of water, 1 part of hydroxy ethyl cellulose, Cellosize QP 4400, and 40 parts of an epoxy resin emulsion having the following composition:

1130 parts low viscosity 100% epoxy resin, epoxy equivalency 170-200, Epotuf ED 1025, 90 parts of polyoxyethylated vegetable oil, Emulphor EL-719, General Aniline & Film Company, and 1,000 parts of water.

The resulting composition was a uniform, thin emulsion free of evidence of agglomeration.

What is claimed is:

1. A liquid composition for forming an adherent corrosion resistant film on a metallic surface which comprises an amine phosphate having the formula:



wherein R_1 and R_2 may each be a member of a class consisting of hydrogen and hydrocarbon radicals having 1 to 12 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl; R_3 is a member of the class consisting of hydrogen and hydrocarbon radicals having 1 to 20 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl; R_4 is a member of a class consisting of H , NH_2 and hydrocarbon radicals having 1 to 20 carbon

atoms, and wherein the foregoing hydrocarbon radicals may contain hydroxyl, bromo, chloro-, sulfo-, nitro-, and amino substituent groups, said phosphate being present in a quantity sufficient to provide an H_3PO_4 equivalency in the range of about 0.05 to about 10, about 1% to about 40% of a film forming resin which is compatible with said phosphate and water in a pH range of about 7 to about 11, said composition containing water and having a pH in the range of about 7 to about 11.

2. A composition as claimed in claim 1 wherein said phosphate is n-butylamine phosphate.

3. A composition as claimed in claim 1 wherein said phosphate is ethylene diamine phosphate.

4. A composition as claimed in claim 1 wherein said resin is an alkyd resin.

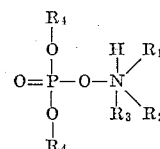
5. A composition as claimed in claim 1 wherein said resin is an epoxy resin.

6. A composition in accordance with claim 1 wherein said amine phosphate is a heterocyclic amine phosphate selected from the group consisting of pyridine phosphate, morpholine phosphate, ring substituted pyridine and ring substituted morpholine phosphates, said ring substituents being a hydrocarbon radical having 1 to 20 carbon atoms and selected from the group consisting of alkyl, aryl and cycloalkyl radicals.

7. A liquid composition in accordance with claim 1 wherein said amine phosphate is the reaction product of said amine and a phosphate selected from the group consisting of zinc phosphate and manganese phosphate.

8. A liquid composition in accordance with claim 7 wherein said reaction product is a zinc-amino complex product containing a ratio of zinc to PO_4 of less than 16.6 to 1.

9. A method for forming and adherent corrosion resistant film on a metallic surface which comprises the steps of applying to said surface a composition comprising an amine phosphate having the formula:



wherein R_1 and R_2 may each be a member of a class consisting of hydrogen and hydrocarbon radicals having 1 to 12 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl; R_3 is a member of the class consisting of hydrogen and hydrocarbon radicals having 1 to 20 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl; R_4 is a member of a class consisting of H , NH_2 and hydrocarbon radicals having 1 to 20 carbon atoms, and wherein the foregoing hydrocarbon radicals may contain hydroxyl, bromo, chloro-, sulfo-, nitro-, and amino substituent groups, said phosphate being present in a quantity sufficient to provide an H_3PO_4 equivalency in the range of about 0.05 to about 10, about 1% to about 40% of a film forming resin which is compatible with said phosphate and water in a pH range of about 7 to about 11, said composition containing water and having a pH in the range of about 7 to about 11, and thereafter heating said coating to a temperature in the range of about 300-450° F. to form an adherent film on said surface.

10. A method as claimed in claim 9 wherein said phosphate is n-butylamine phosphate.

11. A method as claimed in claim 9 wherein said phosphate is ethylene diamine phosphate.

12. A method as claimed in claim 9 wherein said resin is an alkyd resin.

13. A method as claimed in claim 9 wherein said resin is an epoxy resin.

14. A method in accordance with claim 9 wherein said amine phosphate is a heterocyclic amine phosphate selected from the group consisting of pyridine phosphate, morpholine phosphate, ring substituted pyridine and ring substituted morpholine phosphates, said ring substituents being a hydrocarbon radical having 1 to 20 carbon atoms and selected from the group consisting of alkyl, aryl and cycloalkyl radicals.

15. A method in accordance with claim 9 wherein said amine phosphate is the reaction product of said amine and a phosphate selected from the group consisting of zinc phosphate and manganese phosphate.

16. A method in accordance with claim 15 wherein said reaction product is a zinc-amino complex product containing a ratio of zinc to PO_4 of less than 16.6 to 1.

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