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**Hegedus et al.**

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- [54] **CORROSION-RESISTANT ACRYLIC COATINGS**
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- [73] Assignee: **The United States of America as represented by the Secretary of the Navy, Washington, D.C.**
- [21] Appl. No.: **682,154**
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- [51] Int. Cl.<sup>3</sup> ..... **C08L 75/00**

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- [58] Field of Search ..... **524/204, 327, 336, 396**

[56] **References Cited**  
**U.S. PATENT DOCUMENTS**

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[57] **ABSTRACT**

This invention relates to a corrosion-resistant coating capable of being applied to various substrates, e.g., particularly metal and plastic surfaces, as a single coat characterized as having a high-gloss, good adhesion and a high degree of flexibility. The corrosion inhibiting composition comprises an acrylic resin containing an effective amount of a corrosion-inhibiting pigment system consisting essentially of critical amounts of at least one zinc phosphate, zinc molybdate and at least one zinc salt of a benzoic acid.

**15 Claims, No Drawings**

## CORROSION-RESISTANT ACRYLIC COATINGS

## STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the U.S. of America for governmental purposes without the payment of any royalties thereon or therefor.

## CONTINUATION APPLICATIONS

This application is a Continuation-In-Part of copending application Ser. No. 07/627,670 filed Dec. 14, 1990 which in turn is a Continuation-In-Part of copending application Ser. No. 07/593,416 filed Sept. 28, 1990 now U.S. Pat. No. 5,059,640 which in turn is a Continuation-In-Part of copending application Ser. No. 07/442,085 filed on Nov. 28, 1989 now U.S. Pat. No. 5,043,373 which in turn is a Continuation-In-Part of copending application Ser. No. 07/331,200 filed Mar. 28, 1989 now U.S. Pat. No. 4,885,324 which in turn is a Continuation of application 07/211,026 filed June 16, 1988, now abandoned.

## BACKGROUND OF THE INVENTION

This invention relates to coating compositions and more specifically to corrosion-resisting acrylic coating compositions which can be applied by various methods directly onto surfaces and particularly metal surfaces and polymeric or plastic substrates without the need for an undercoat.

Metal substrates, and particularly metal exposed to extreme environmental conditions, require the protection of coatings capable of resisting corrosion e.g., ships and military aircraft exposed to seawater spray and other corrosive reagents including acid-forming gases, e.g. sulfur dioxide and the like. In addition to ships and aircraft, particularly military aircraft, various types of machinery and farm equipment used in industrial environments where fossil fuels generate corrosive agents need protection against various reagents. In addition to corrosion, it is important that the coatings have physical characteristics which enable the coating to be applied to the substrate without difficulty. These coatings should also exhibit good adhesion and have a high degree of flexibility.

Presently, coatings attempting to comply with the above-mentioned requirements rely on the use of a plurality of films, i.e. an undercoat with a topcoat, comprising, for example, an epoxy undercoat and a polyurethane topcoat. The epoxy primers used in the military are specifically designed to adhere to metal surfaces. Many of the primers, however, generally require a topcoat, since the primers do not have the required flexibility, particularly at low temperatures, and therefore results in extensive cracking and/or blistering in areas which are highly flexible. Moreover, the primer coats are not generally resistant to harsh weather conditions and are difficult to formulate in the multi-colors required for military aircraft. The acrylic coating compositions of this invention are resistant to harsh weather conditions and various chemicals including saltwater and have the required degree of flexibility. In addition, it was necessary heretofore to provide a plurality of films of the coatings to form a total film thickness ranging up to about 0.005 inches e.g. up to 10 mils or greater which adds considerable weight. Thus, the multi-coat finishes require a plurality of films which are very time consuming in applying because of the drying time be-

tween each application. Moreover, it is obvious that the removal of the two coat system can likewise be difficult and time consuming and requires the use of large amounts of organic solvents causing objectionable emissions.

In accordance with this invention, the corrosion resistant coatings comprise an acrylic binder, i.e. an acrylic resin such as Acryloid AU-608S or 608X. These particular acrylic resins are acrylic polyols designed to produce hard, resistant, desirable coatings when reacted with isocyanates. More specifically, the coating compositions of this invention comprises approximately 100 parts by weight of an acrylic resin in combination with about 0 to 1000 parts by weight of at least one organic paint solvent for said resin and from about 10 to 140 parts by weight of a TiO<sub>2</sub> pigment, e.g. titanium dioxide pigment in the form of vesiculated beads or combinations of TiO<sub>2</sub> beads and pigment and from about 0.01 to 300 parts by weight of a combination of corrosion-inhibiting pigments consisting essentially of about 10 to 120 parts by weight of at least one zinc phosphate, 40 to 260 parts by weight of zinc molybdate, and 1 to 30 parts by weight of at least one zinc salt of a benzoic acid, e.g. substituted zinc benzoate. For purposes of this invention, all three of the zinc salts, as disclosed herein, are essential in their relative proportions to provide the corrosion resistance required for coatings. Other pigments, and particularly, spherical TiO<sub>2</sub> particles and the vesiculated beads e.g. TiO<sub>2</sub> beads may be used in combination with the three zinc salts as disclosed herein.

The coating composition of this invention may be applied as a single coat directly onto a hard surface such as metal, plastic or polymeric surfaces and do not require a top coat to provide a high gloss, corrosion resistant film. It is generally known that low gloss coatings are appropriate for camouflage purposes particularly on most of the outer exposed surfaces of military aircraft and the like. On the other hand, low gloss coatings are not appropriate for the internal or unexposed surfaces such as the areas around engine inlets, ducts, landing gears, etc. Moreover, aircraft other than the military aircraft, require high gloss and high visibility coatings. It was therefore believed that in order to obtain a coating which would exhibit outstanding corrosion resistance, the amount of pigment, i.e. (PVC) pigment volume concentration had to be relatively high which would therefore result in a low gloss finish. It was believed that it was not possible to obtain a final coat which also had high gloss and good corrosion resistance at high pigment volume concentrations.

## SUMMARY OF THE INVENTION

This invention relates to a corrosion-resistant coating capable of being applied to various substrates as a single coat having high-gloss, good adhesion and a high degree of flexibility. The corrosion inhibiting coating comprises an acrylic resin and a corrosion inhibiting pigment system consisting essentially of critical amounts of zinc phosphate, zinc molybdate and at least one zinc salt of a benzoic acid.

It is an object of this invention to provide a glossy, corrosion-resistant coating, which can be applied directly onto a surface without the need for an undercoat.

It is another object of this invention to provide a coating which is resistant to corrosion and various other chemicals, is flexible, resistant to different weather conditions and has good adhesion to metal substrates.

It is still a further object of this invention to provide a corrosion resistant coating capable of reducing the time, the manpower and the materials normally required for applying said coating on various substrates.

It is still a further object of this invention to provide a one-coat system useful for both military and civilian aircraft of substantially reduced thickness which reduces the weight added to the aircraft while at the same time providing the necessary corrosion resistance.

These and other objects of the invention are accomplished by providing an acrylic resin containing an unique combination of pigments which can be applied on a variety of substrates.

#### DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a relatively high-gloss, corrosion resistant coating composition which functions as the primary coat or topcoat, has good adhesion characteristics, is highly flexible and resistant to chemical and corrosive environments. More specifically, this invention is directed to a relatively high-gloss, corrosion-resistant coating which comprises for each 100 parts by weight of an acrylic resin, e.g., an acrylic-urethane resin from about 0 to 1000 parts by weight of at least one organic paint solvent and preferably from about 50 to 500 parts by weight of solvent including xylene, toluene, mineral spirits and combinations thereof, and from about 0 to 140 parts by weight of  $TiO_2$  pigment e.g., preferably from about 40 to 100 parts by weight of  $TiO_2$  pigment. The  $TiO_2$  pigment may consist of from about 0 to 100 per cent by weight of the total amount of  $TiO_2$  of vesiculated beads.

In addition to the above, the coating composition must contain from about 0.1 to 300 parts by weight and preferably from about 20 to 100 parts by weight of a combination of corrosion inhibiting pigments consisting essentially of about 10 to 100 parts by weight of at least one zinc phosphate, 40 to 260 parts by weight of zinc molybdate, and 1 to 30 parts by weight of at least one zinc salt of a benzoic acid, e.g. zinc benzoate and/or a zinc salt of a substituted benzoic acid wherein the substituents include  $NO_2$  and/or hydroxy radicals.

The acrylic polymers, useful for purposes of this invention, include copolymers, and terpolymers of methacrylic and acrylic acid which contain up to about 15 weight percent of carboxyl functionality. For example, polymers derived from acrylates, e.g. methyl methacrylate and acrylic and methacrylic acid may have molecular weights ranging up to about 500,000. The acrylic resins may be provided in solution at concentrations ranging up to 60% by weight, and therefore it may not be necessary to add additional solvent. However, various solvents may be used in preparing the coating including xylene, toluene, mineral terpene, methyl ethyl ketone, methyl isobutyl ketone, ethyl cellosolve, butyl cellosolve, cellosolve acetate, ethyl acetate, butyl acetate, methyl isobutyl carbinol, isopropanol, n-butanol, cyclohexanone or mixtures thereof in any proportion. Usually, the content of the non-volatile components in the coating composition of this invention ranges up to about 90% e.g., 25-50% by weight of the total composition. The amount of solvent may vary depending on the viscosity and method of application of the coating.

The pigment system of this invention is unique in that it consists essentially of at least one zinc phosphate, e.g. zinc-barium phosphate, a zinc salt of benzoic acid or a substituted benzoic acid and zinc molybdate. These

three zinc pigments alone or in combination with other known pigments, e.g.  $TiO_2$ , provide a coating having outstanding corrosion inhibiting characteristics which enables a single film of the coating to be used as a primer or as the topcoat.

Of the various zinc salts of benzoic acids, it was found that the preferred zinc benzoates include the benzoic acid salts having at least one substituent, i.e. the hydroxyl and/or the nitro ( $NO_2$ ) substituent. The preferred zinc phosphates, e.g. zinc-barium phosphate, are commercially available as Phos-Plus (J0866) from the Minerals Pigment Corporation. The zinc molybdates are well known zinc compounds commercially available as Moly-White. In addition to the zinc salts pigment system as disclosed herein, other known pigments, particularly titanium dioxide, zinc oxide and the like may be used in the coating to provide reinforcing characteristics and to add color, opacity and hiding power to the coating. In addition, other additives well known in the coating art such as color or tinting agents may be added to the binder in small but effective amounts and include such compounds as antimony oxides, barium sulfate, calcium carbonates and one or more of the organic pigments such as the phthalocyanine colors, e.g. greens or blues, etc.

It was unexpected that the combination of zinc molybdate, the zinc salts of benzoic acid and the zinc phosphates synergistically improved the corrosion resistance of the coating even at low concentrations. It was found that the specific combination of the zinc molybdate, zinc salts of benzoic acid and zinc phosphates in the relative ratios stated herein improved the corrosion-resistance substantially when compared to the use of either one of these zinc salts alone. Thus, by decreasing the pigment volume concentration (PVC) of the pigment system in the acrylic binder, a coating of higher gloss can be obtained without impairing the corrosion resistance.

In general, the coatings are prepared by mixing all of the ingredients into the acrylic binder and applying the film-forming composition to the substrate at thicknesses ranging from about 0.001 to 0.005 inches up to about 20 mils and preferably from about 1 to 10 mils. A dispersion or solution of the coating may be accomplished by conventional mixing methods including the use of agitation with a mixer, ball mills, etc. The application of the coating onto the substrate e.g. metal surface, may be made by known coating procedures such as spraying, dipping, brushing, roller coating, etc. The viscosity of the coatings for the particular application may be adjusted by the addition of one or more known organic solvents within the numerical ranges disclosed herein. After the coating is applied to the surface, the solvent is allowed to evaporate at room or elevated temperatures and the film cures to a coating having the desired characteristics.

The particular zinc phosphate used in preparing the coating composition has an average particle size of about 5.0 microns and may be characterized as a zinc-barium phosphate. The zinc salts of benzoic acid are specifically characterized as having at least one hydroxyl group and/or nitro ( $NO_2$ ) substituent with a molecular weight of about 100-500, a density of about 2-3 grams per milliliter and a particle specific surface area of  $16m^2/gram$ . The benzoic acid salts are commercial products obtained from BASF and identified as Sicorin-RZ. The zinc molybdate has a particle size of about 2 microns and is commercially available as

Moly-White 101. The titanium dioxide is preferably spherical with a particle size of about 0.25 microns. The term zinc phosphates includes the mixed zinc salts and particularly the zinc-barium phosphates, zinc-aluminum phosphates and various combinations of zinc phosphate with mixed zinc phosphate salts in any proportion.

The coating composition may optionally contain other additives such as an ultraviolet light stabilizer, antioxidants or both. The ultraviolet light stabilizer can be present in amounts of 1-10% by weight, based on the weight of the binder; the antioxidant can be present in amounts of 0.1-3% by weight, based on the weight of the binder. Typical ultraviolet light stabilizers are benzophenones, triazines, triazines, substituted benzenes, organophosphorous sulfides, and substituted nitriles. The coating composition of this invention may also contain other known materials, such as driers, antioxidants, fungicides, etc. in amounts for their intended function with various solvents for such materials. Organic salts (e.g., an octoate or naphthenate) of metals (e.g., cobalt, calcium, zirconium, manganese, bismuth or antimony) are available from Nuodex Corporation under the name "Nuxtra". The coating composition may also contain fillers which may or may not have pigmentary properties. These fillers are exemplified by talc, silica, barium sulfate, calcium sulfate, calcium carbonate, calcium silicate, iron oxides, mica, aluminum silicate, clay and mixtures thereof.

The coating composition can be applied to a variety of substrates by any of the conventional methods. Substrates include, for example, metal, wood, glass, or plastics such as polypropylene, polystyrene, and the like. The coating is suited also for application over pre-treated or unpripped metal.

The hydrocarbon solvents useful for purposes of this invention includes a mixture of solvents, e.g. mixtures of one or more paint solvents such as benzene, toluene, xylene, and aromatic naphtha. Other solvents include the ester solvents such as ethyl acetate, butyl acetate, cellosolve, hexyl acetate, amyl acetate, ethyl propionate, and butyl propionate. Ketone solvents include acetone, methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, diethyl ketone, and cyclohexanone. Glycol ester solvents include ethylene glycol monoethyl ether acetate, diethylene glycol monoethyl ether acetate, etc.

The coating has outstanding performance when exposed to high intensity of light, extreme cold conditions, hot lubricating oils and other chemicals normally found in aircraft operations. By utilizing the coating composition of this invention, a high gloss corrosion resistant film can be obtained on various substrates as the top coat. The coating has properties which function as a primer and more important as a top coat highly adherent, flexible, chemical resistant and resistant to all weather conditions. The coatings of this invention lowers the risk of failure due to cracking especially at low temperatures and are easily touched-up since only one coating need be applied. Since one coat is sufficient, it needs less time for application and removal which saves on manpower that would generally be needed in the preparation of a high gloss two coat system. Moreover, the present coating provides protection at lower film thicknesses thereby reducing the weight of the coating compared to a two coat paint system which is important for aircraft coatings.

The following illustrate the coating compositions of this invention.

EXAMPLE I ACRYLIC RESIN	
Components	Parts by Weight
Acrylic resin (60% solids) (AU-6085)	55.0
TiO <sub>2</sub> (50% VSBD)	28.9
Zinc Phosphate	2.9
Zinc Benzoate	0.3
Zinc Molybdate	5.9
Organic Solvents	7.0
	100.0

The above composition has the following characteristics:

PVC =	0.11
Wet Density (g/ml) =	1.44
Weight % Solids =	0.709
VOC (g/l) =	419.93

The degree of anti-corrosion performance of the coating can be measured by ASTM test D610-68 entitled "Evaluating Degree of Rusting on Painted Steel Surfaces", ASTM D1654-79a entitled "Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments", and ASTM D714-56 entitled "Evaluating Degree of Blistering of Paints". The coating can be tested further in ASTM B117-73, entitled "Method of Salt Spray (Fog) Testing" wherein the composition is applied onto steel panels which are scribed and subjected to salt-fog spray. Scribing is achieved by scratching an "X" in the coating through to bare steel using a cutting tool. The amount of rusting at the scribe is assessed on a scale of 0-10 where 10 is no corrosion and 0 is complete failure. Ratings of 5 and above are acceptable for anti-corrosive compositions tested in accordance with ASTM D-1654-79.

Scribe creepage or underfilm corrosion is determined in accordance with ASTM D1654-79a on a scale of 0-10 where 10 is no corrosion and 0 is  $\frac{1}{4}$  inch or more creepage from the scribe. Ratings of 3 or above are acceptable for anti-corrosive compositions. Blistering in a coating is determined in accordance with ASTM D714-56. This method describes blister size as numbers 2, 4, 6, 8, and 10, where 2 is a large blister  $\frac{1}{4}$  inch or larger in diameter, 8 is a small blister less than  $\frac{1}{16}$  inch in diameter and 10 is the absence of blistering.

It is obvious that there are other variations and modifications which can be made with respect to this invention without departing from the spirit and scope of the invention as particularly set forth in the appended claims.

The invention claimed:

1. A coating composition comprising about 100 parts by weight of an acrylic resin from about 0 to 1000 parts by weight of at least one organic solvent, from about 0-140 parts by weight of a TiO<sub>2</sub> pigment, and from about 0.01 to 300 parts by weight of a combination of corrosion-inhibiting pigments consisting essentially of about:

- 10-120 parts by weight of a zinc phosphate,
- 40-260 parts by weight of zinc molybdate, and
- 1-30 parts by weight of at least one zinc salt of a benzoic acid.

2. The coating composition of claim 1 further characterized in that the salt is a substituted zinc benzoate.

3. The coating composition of claim 1 further characterized in that the zinc phosphate is a zinc-barium phosphate.

4. The coating composition of claim 1 further characterized in that from 0 to 100% by weight of the total amount of the TiO<sub>2</sub> pigment in the coating is in the form of vesiculated beads.

5. The coating composition of claim 1 further characterized in that from 10 to about 50% by weight of the total amount of the TiO<sub>2</sub> pigment in the coating is in the form of vesiculated beads.

6. The coating composition of claim 4 further characterized in that the TiO<sub>2</sub> pigment is present in the coating in an amount ranging from about 40-100 parts by weight.

7. The coating composition of claim 1 further characterized in that the combination of corrosion-inhibiting pigments is present in an amount ranging from about 20 to 100 parts by weight.

8. The coating composition of claim 1 further characterized in that the acrylic resin is an acrylic-urethane resin and the combination of corrosion-inhibiting pigments consist essentially of about:

- (a) 30-100 parts by weight of a zinc-barium phosphate,
- (b) 60-210 parts by weight of a zinc molybdate, and
- (c) 3-25 parts by weight of a zinc salt of a benzoic acid.

9. The coating composition of claim 8 further characterized in that the zinc salt of the benzoic acid is a substituted benzoic acid.

10. The coating composition of claim 9 further characterized in that the substituted benzoic acid is a hydroxy and NO<sub>2</sub>-substituted benzoic acid.

11. The coating composition of claim 9 further characterized in that the substituted benzoic acid is a NO<sub>2</sub>-substituted benzoic acid.

12. A method of preparing a corrosion-inhibiting coating which comprises adding to an acrylic resin from about 0.01 to 300 parts by weight for every 100 parts by weight of resin of a combination of pigment consisting essentially of from about 10 to 120 parts by weight of a zinc phosphate, 40 to 260 parts by weight of zinc molybdate and 1 to 30 parts by weight of at least one zinc salt of benzoic acid.

13. The method of claim 12 further characterized in that from about 50 to 500 parts by weight of at least one organic solvent is present for each 100 parts by weight of said acrylic resin.

14. The method of claim 13 further characterized in that the coating contains from about 0 to 140 parts by weight of TiO<sub>2</sub> pigment.

15. The method of claim 14 further characterized in that the zinc phosphate is a zinc-barium phosphate and 10 to 50 percent by weight of the total amount of TiO<sub>2</sub> pigment is in the form of vesiculated beads.

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