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CORROSION RESISTANT VINYL COATED METAL ARTICLES

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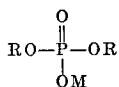
Int. Cl. C23f 7/10

U.S. Cl. 148—6.15 R

6 Claims

ABSTRACT OF THE DISCLOSURE

Vinyl coated metal articles are rendered corrosion resistant by applying thereon an alkali metal dialkyl phosphate of the formula:

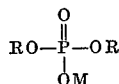


wherein R is an alkyl group containing from about 8 to about 16 carbon atoms inclusive, and M is an alkali metal ion.

RELATED APPLICATION

This application is a division of application Ser. No. 747,095, filed July 24, 1968 now abandoned.

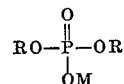
This invention relates to vinyl coated metal articles having deposited thereon an alkali metal dialkyl phosphate. More particularly, it relates to vinyl coated exterior automotive roof coverings which are rendered corrosion resistant when applied to the metal roof by having coated thereon a minor but effective amount sufficient to inhibit corrosion of an alkali metal dialkyl phosphate of the formula:



wherein R is an alkyl group containing from about 8 to about 16 carbon atoms inclusive, and M is an alkali metal ion.

As is well known, polyvinyl chloride resin is subject to deterioration by both heat and ultraviolet light. While a number of stabilizers have been employed to inhibit these deleterious effects, the recent practice of coating metal articles with polyvinyl chloride coated fabric requires the provision of stabilizers which inhibit corrosion on the metal surface as well as inhibit decomposition of the vinyl chloride resin. These problems are particularly troublesome for automobiles having vinyl hard tops as these automobiles are often subject to severe weather conditions. Accordingly, within a short time after application, rust develops between the metal substrate and the polyvinyl chloride coated fabric. Although the vinyl car top application is a relatively new application, it has become very popular and presently represents a substantial proportion of total production. Accordingly, it has become highly desirable that a solution to this corrosion problem be provided.

In accordance with this invention, it has been discovered that the aforesaid problems can be obviated or substantially reduced by incorporating with the vinyl chloride metal article, a minor but effective amount sufficient to inhibit corrosion of an alkali metal dialkyl phosphate of the formula:



wherein R is an alkyl group containing from about 8 to

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about 16 carbon atoms inclusive, and M is an alkali metal ion.

Illustrative of the alkali metal ions are sodium lithium and potassium. While ammonium is not truly a member of the alkali metal series, it is a clear equivalent for the alkali metal ions and is generally considered to be within the term of an equivalent of alkali metals. It is so considered in the present case. Sodium ions and ammonium ions are preferred in the present invention because of their low cost and efficiency. Illustrative of the alkyl groups as represented by the substituent R are octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl and the like, or mixtures thereof. Of these substituents represented by R, decyl has been found to be preferred as such compounds provide exceptional corrosion inhibiting properties. Particularly preferred for similar reasons are the branched decyl groups wherein the decyl group is derived from a highly branched primary alcohol.

In accordance with this invention, the alkali metal dialkyl phosphate can be applied to the metal surface, to the polyvinyl chloride resin, or preferably to a fabric which is to be coated with polyvinyl chloride resin. Although the alkali metal dialkyl phosphate inhibitor can be applied in concentrated form, it is preferred that it be dissolved in a suitable solvent. Exemplary of suitable solvents are the petroleum hydrocarbons, such as naphtha; the aromatic hydrocarbons such as, benzene; the chlorinated hydrocarbons such as, perchlorethylene; and the alcohols such as, methanol, ethanol, or hexylene glycol. If desired, the phosphate inhibitor can also be employed with water in which it is sparingly soluble but forms a stable emulsion. The amount of alkali metal dialkyl phosphate inhibitor can vary from about 25 p.p.m. to about 100% based on the concentration of aqueous or hydrocarbon solvent. Generally, however, an inhibitor concentration of from about 0.05% to about 20% is preferred for reasons for economy.

While the inhibitor can be employed to advantage with any metal substrate, the inhibitors are particularly effective with ferrous metals.

The vinyl chloride resins useful in the practice of this invention are polyvinyl chloride resin and copolymers of at least 70% of vinyl chloride and up to 30% of other polymerizable mono-olefinic monomers compatible with vinyl chloride. Examples of compatible monomers include: vinyl carboxylate esters, e.g., vinyl acetate, and other vinyl esters of mono carboxylic acids particularly those having from one to five carbon atoms; maleic and fumaric acids as well as the alkyl esters such as ethylmaleate and ethylfumarate; alkyl esters of acrylic acids, particularly those wherein the alkyl radical has from one to four carbon atoms such as ethyl and methyl acrylate; as well as acrylic and methacrylic acids; maleic anhydride; itaconic and aconitic acids and vinylidene chloride. These polymers and copolymers can be prepared by any of the well-known methods such as, polymerization in aqueous emulsion.

The vinyl resin can be employed with or without stabilizer but preferably the stabilized vinyl resin is employed. Exemplary of suitable stabilizers are the organic phosphites, metallic soaps such as calcium or zinc stearate, fatty acids such as stearic acid, phenolic compounds including substituted phenols, barium or cadmium phenolates, phosphinates, phosphonates, mercaptides and sulfides, epoxidized fatty oils, episulfides and epoxides, indoles, lead soaps, including lead naphthenates, polyols, such as sorbitol or pentaerythritol, esters of aminocrotonic acid, dialkyltin carboxylates or mercaptides, alkylstannic acids, urea or thiourea derivatives, as well as other additives, known in the art of polyvinyl polymer stabilization

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to include fillers such as carbon black and titanium dioxide, etc.

For use as car tops, one suitable method of application is as follows: The vinyl resin is applied to a fabric such as cotton sateen, cotton drill, rayon sateen, polyester/cotton blended fibers drill, etc., and bleached and finished with a fluorinated hydrocarbon type water repellent, such as Du Pont Zepel D. The fabric is then calender coated with a solid-plasticized and pigmented polyvinyl chloride resin composition. A topcoat consisting of a solvent solution (methyl-ethyl ketone solvent) of polyvinyl chloride and polymethyl methacrylate resins is roller knife coated onto the calendered vinyl. The construction is then embossed in the desired grain, trimmed and applied with adhesive to the hard top.

The following examples will serve to illustrate the invention and its preferred embodiments. All parts and percentages are by weight unless otherwise specified.

Example 1

In accordance with the conventional procedure, samples of cotton sateen, cotton drill, cotton osnaburg, rayon sateen, rayon drill and polyester cotton drill were sprayed on one side with a polyvinyl chloride emulsion grade resin (Geon 121). The resin was stabilized with a mixture of barium-cadmium phenolates, organic phosphites, and calcium-zinc stearate; and plasticized with dioctyl phthalate. The resin which contained 50 parts plasticizer, 30 parts calcium carbonate filler, and 5-6 parts stabilizer per 100 parts resin was applied in a concentration of approximately 16 ozs. per square yard of fabric. The fabrics were sprayed with from between 1.11 grams and 1.56 grams (dry weight) of adhesive and allowed to dry for 20 minutes at room temperature. The fabrics measuring 8 inches by 8 inches were then applied to adhesive coated unpainted steel 10 inch by 10 inch panels, having sprayed thereon between 1.73 to 2.43 grams (dry weight) of the same adhesive, 30 seconds after application. The assemblies were allowed to air dry for approximately 16 hours at room temperature and then placed in a wooden rack in the vertical position. The racks were placed into an air circulating oven for 10 minutes at a temperature of approximately 240° F. until the surface temperature of the vinyl cover was between 180° F. and 185° F. The samples were then taken from the oven and immediately immersed in water for 2 minutes, the water temperature not exceeding 75° F. The samples were allowed to dry for 48 hours at room temperature and then the immersion and drying steps were repeated. The samples were then inspected for rust by visual inspection, and rust was observed.

The test was then repeated but for the exception that fabrics were sprayed on one side with 55% solution of sodium didecyl phosphate dissolved in naphtha until the surface was visibly wet. The fabrics were then allowed to air dry and coated with the vinyl resin on the side not treated with the phosphate and then tested in accordance with the aforesaid procedure. Upon visual examination, no rust was noted on the treated sample.

Example 2

In accordance with the previous example, a 5% solution of sodium didecyl phosphate dissolved in naphtha was employed and no rust formation was noted.

Example 3

In accordance with the previous examples, sodium dioctyl phosphate is employed as the stabilizer and the results are in general agreement with Examples 1, and 2.

Example 4

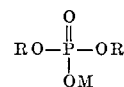
In accordance with the previous examples, the tests are repeated but for the exception that the phosphate inhibitor is applied to the metal substrate. No rust formation is noted on the phosphate treated articles.

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Although the phosphate inhibitor can be applied to the metal, to the vinyl resin or to a fabric which is later coated with the vinyl resin, the latter method is preferred when the vinyl resin is to be applied to an automobile roof. While the exact mechanism of the invention is not known, it is known that moisture gets between the fabric and the metal and that nearly all of the materials employed tend to corrode or promote corrosion. Exemplary of these latter materials, are the water repellents such as the fluorinated hydrocarbons and even the commonly employed adhesives contain chemicals which promote corrosion.

What is claimed:

1. A corrosion resistant article consisting essentially of a ferrous metal substrate, a vinyl chloride resin bonded with adhesive to a surface thereof, said vinyl chloride resin containing a minor but effective amount of a corrosion inhibitor sufficient to inhibit corrosion of the metal substrate at the bond interface, said corrosion inhibitor being an alkali metal dialkyl phosphate of the formula:

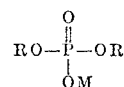


wherein R is an alkyl group containing from 8 to 16 carbon atoms, inclusive, and M is an alkali metal ion.

2. A corrosion resistant article of claim 1 wherein the phosphate is sodium didecyl phosphate.

3. A corrosion resistant article of claim 1 wherein the phosphate is sodium dioctyl phosphate.

4. A corrosion resistant metal article consisting essentially of a ferrous metal substrate having bonded thereto with adhesive a water repellent fabric having coated thereon at the bond interface a minor but effective amount of a corrosion inhibitor sufficient to inhibit corrosion of said metal substrate at said bond interface, said corrosion inhibitor being an alkali metal dialkyl phosphate of the formula:



wherein R is an alkyl group containing from 8 to 16 carbon atoms, inclusive, and M is an alkali metal ion, said fabric having coated thereon on the side opposite the bond interface a vinyl chloride resin.

5. A corrosion resistant article of claim 4 wherein the phosphate is sodium didecyl phosphate.

6. A corrosion resistant article of claim 4 wherein the phosphate is sodium dioctyl phosphate.

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RALPH S. KENDALL, Primary Examiner

U.S. Cl. X.R.

252—389; 161—218; 260—45.7 P