METHOD FOR TREATING AND/OR COATING A SUBSTRATE WITH NON-CRÖMÊ MATERIALS

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ABSTRACT

The present invention is directed to a method for coating a substrate comprising: (a) applying a caustic cleaner onto at least a portion of the substrate; (b) rinsing at least a portion of the substrate that was subjected to step (a) with water; (c) applying an acid cleaner onto at least a portion of the caustically cleaned substrate; (d) rinsing at least a portion of the substrate that was subjected to step (c) with water; and (e) applying a conversion coating comprising zirconium onto at least a portion of the acid cleaned substrate; and wherein at least one of the materials used in steps (c) and (e) is substantially chrome free. The present invention is also directed to a substrate, such as an aluminum substrate, that has been coated using the aforementioned method.
METHOD FOR TREATING AND/OR COATING A SUBSTRATE WITH NON-CHROME MATERIALS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

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FIELD OF THE INVENTION

The present invention relates generally to a method for treating and/or coating a substrate with non-chrome materials.

BACKGROUND INFORMATION

Conventional pretreatment and primer coating compositions which are used in the aerospace industry contain chrome, such as hexavalent chrome, in order to impart corrosion resistance to the substrate onto which these coatings are deposited. However, due to toxicity concerns associated with hexavalent chrome as well as potential governmental regulations regarding the amount of hexavalent chrome that may be used in a coating, there is a need to reduce and/or eliminate that use of hexavalent chrome in pretreatment and primer coatings that are used in the aerospace industry.

SUMMARY OF THE INVENTION

The present invention is directed to a method for coating a substrate comprising: (a) applying a caustic cleaner onto at least a portion of the substrate; (b) rinsing at least a portion of the substrate that was subjected to step (a) with water; (c) applying an acid cleaner onto at least a portion of the caustically cleaned substrate; (d) rinsing at least a portion of the substrate that was subjected to step (c) with water; and (e) applying a conversion coating comprising zirconium onto at least a portion of the acid cleaned substrate; and wherein at least one of the materials used in steps (c) and (e) is substantially chrome free. The present invention is also directed to a substrate, such as an aluminum substrate, that has been coated with the aforementioned method.

The present invention is also directed to a method for coating a substrate comprising: (a) applying a caustic cleaner onto at least a portion of the substrate; (b) rinsing at least a portion of the substrate that was subjected to step (a) with water; (c) applying an acid cleaner onto at least a portion of the caustically cleaned substrate; (d) rinsing at least a portion of the substrate that was subjected to step (c) with water; and (e) applying a conversion coating comprising zirconium onto at least a portion of the acid cleaned substrate; and wherein the materials used in steps (c) and (e) are substantially chrome free.

The present invention is also directed to a method for coating a substrate consisting essentially of: (a) applying a caustic cleaner onto at least a portion of the substrate; (b) rinsing at least a portion of the substrate that was subjected to step (a) with water; (c) applying an acid cleaner onto at least a portion of the caustically cleaned substrate; (d) rinsing at least a portion of the substrate that was subjected to step (c) with water; (e) applying a conversion coating comprising zirconium onto at least a portion of the acid cleaned substrate; (f) rinsing at least a portion of the substrate that was subjected to step (e) with water; and (g) applying an electrodepositable coating composition onto at least a portion of the conversion coating, wherein the electrodepositable coating composition comprises a corrosion inhibitor; and wherein the materials used in steps (c), (e), and (g) are substantially free of chrome.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, unless otherwise expressly specified, all numbers such as those expressing values, ranges, amounts or percentages may be read as if prefaced by the word "about", even if the term does not expressly appear. Plural encompasses singular and vice versa. For example, although reference is made herein to "a" caustic cleaner, "an" acid cleaner, "a" conversion coating, "an" electrodepositable coating, "a" corrosion inhibitor, a combination (i.e., a plurality) of caustic cleaners and acid cleaners may be used.

As used herein, "plurality" means two or more.

As used herein, "includes" and like terms means "including without limitation".

When referring to any numerical range of values, such ranges are understood to include each and every number and/or fraction between the stated range minimum and maximum.

As used herein, the term "cure" refers to a coating wherein any crosslinkable components of the composition are at least partially crosslinked. In certain embodiments, the crosslink density of the crosslinkable components (i.e., the degree of crosslinking) ranges from 5% to 100%, such as 35% to 85%, or, in some cases, 50% to 85% of complete crosslinking. One skilled in the art will understand that the presence and degree of crosslinking (i.e., the crosslink density) can be determined by a variety of methods, such as dynamic mechanical thermal analysis (DMTA) using a Polymer Laboratories MK III DMTA analyzer conducted under nitrogen.

As used herein, molecular weight refers to number average molecular weight (Mn) as determined by Gel Permeation Chromatography.

Reference to any monomer(s) herein refers generally to a monomer that can be polymerized with another polymerizable compound such as another monomer or polymer. Unless otherwise indicated, it should be appreciated that once the monomer components react with one another to form the compound, the compound will comprise the residues of the monomer components.

Coating Process

As stated above, the present invention is directed to a method of coating a substrate, such as an aluminum substrate, with a non-chrome coating system. Unlike other methods of coating an aluminum substrate, the method disclosed herein does not require the use of any materials (e.g., cleaners, water, conversion coatings, electrodepositable coating compositions) that contain chrome. Accordingly, in certain embodiments, the materials used in one or more of the steps described below can be substantially chrome free. As used herein, "substantially chrome free" means that chrome is not intentionally added to the material by the user. For example, in some embodiments, all the materials used in the steps described below are substantially chrome free. In other embodiments, one or more of the materials used in the steps below (e.g., the conversion coating and/or the electrodepositable coating composition) are substantially chrome free while other materials used in other steps (e.g., the acid...
cleaner) may contain chrome. For purposes of this disclosure, the materials used in steps (a) through (g) may be applied onto the substrate using techniques known in the art such as spray and/or immersion techniques. [0015] The method begins by (a) applying a caustic cleaner onto at least a portion of a substrate. The caustic cleaner is used to remove oil and/or other contaminants (e.g., dirt or dust), which can be deposited onto the surface of the substrate during a forming and/or stamping process, prior to the application of another coating composition onto the substrate. The caustic cleaner that may be used in the present invention can be any silicate and/or non-silicate caustic cleaners known in the art. Suitable silicate and/or non-silicate caustic cleaners include METALAST CLEANER 1000 (commercially available from METALAST International, Inc.), RIDOLENE 298 (commercially available from HENKEL), CHEMKLEEN 275 (commercially available from PPG Industries, Inc.), or combinations thereof.

[0016] After step (a), at least a portion of the substrate that was subjected to step (a) undergoes (b) a rinsing stage and rinsed with water, such as deionized water, in order to wash at least a portion of the caustic cleaner from the surface of the substrate.

[0017] After step (b), (c) an acid cleaner is applied onto at least a portion of the caustically cleaned substrate. The acid cleaner is applied onto the surface in order to etch the surface of the substrate. In certain embodiments, the acid cleaner is used to deoxidize the surface of the substrate (e.g., remove the oxide layer found on the surface of the substrate) in order to promote the uniform deposition of a conversion coating, which is described below, as well as to promote the adhesion of the conversion coating to the substrate. Suitable acid cleaners that may be used in the method disclosed herein include, without limitation, phosphoric acid, sulfuric acid, nitric acid, hydrofluoric acid, LINC DEOXIDIZER (commercially available from Oakite), TURCO DEOXIDIZER 6 (commercially available from Henkel), or combinations thereof.

[0018] After step (c), at least a portion of the substrate that was subjected to step (c) undergoes (d) a rinsing stage and rinsed with water, such as deionized water, in order to wash at least a portion of the acid cleaner from the surface of the substrate.

[0019] After step (d), (e) a conversion coating composition (pretreatment coating composition) comprising zirconium is then deposited onto at least a portion of the acid cleaned substrate. In some embodiments, the conversion coating comprises a pretreatment bath that comprises 10 parts per million (ppm) to 10,000 ppm of zirconium based on the total weight of the pretreatment bath. In certain embodiments, the conversion coating composition can further comprise chrome. Traditional chrome containing (non-zirconium containing) conversion coatings, which are known in the art, may also be used in the present invention. Examples of such traditional chrome containing conversion coatings include ALODINE 1200S (commercially available from Henkel) and/or METALAST TCP-HF (commercially available from Metalast International Inc.).

[0020] Alternatively, in some embodiments, in lieu of the application of the conversion coating described in the previous paragraph, the surface of the substrate can be anodized using techniques known in the art.

[0021] After step (e), at least a portion of the substrate that was subjected to step (c) undergoes (f) a rinsing stage and rinsed with water, such as deionized water, in order to wash at least a portion of excess conversion coating composition from the surface of the substrate.

[0022] After step (f), (g) an electrodeposited coating composition, which comprises a corrosion inhibitor, is deposited onto at least a portion of the substrate onto which the conversion coating was deposited using techniques known in the art such as anodic or cathodic electrodeposition. In some embodiments, the electrodeposited coating composition is an anionic electrodepositable coating composition. In certain embodiments, suitable corrosion inhibitors that may be used in the electrodepositable coating composition comprise a nitrogen-containing heterocyclic compound. Examples of such compounds, which are suitable for use in the present invention, are azoles, oxazoles, thiazoles, thiazolines, imidazoles, diazoles, pyridines, indazolines, and triazines, tetrazoles, toltriazole, or mixtures thereof. Suitable triazoles include, for example, 1,2,3-triazole, 1,2,4-triazole, benzotriazole, and their derivatives, or combinations thereof. Derivatives of 1,2,3-triazole, which are suitable for use in the present invention, include 1-methyl-1,2,3-triazole, 1-phenyl-1,2,3-triazole, 4-methyl-2-phenyl-1,2,3-triazole, 1-benzyl-1,2,3-triazole, 4-hydroxy-1,2,3-triazole, 1-amino-1,2,3-triazole, 1-benzamido-4-methyl-1,2,3-triazole, 1-amino-4,5-diphenyl-1,2,3-triazole, 1,2-diphenyl-1,2,3-triazole, 1,2-triazole aldehyde, 2-methyl-1,2,3-triazole-4-carboxylic acid, and 4-cyano-1,2,3-triazole, or combinations thereof. Derivatives of 1,2,4-triazole, which are suitable for use in the present invention, include 1-methyl-1,2,4-triazole, 1,3-diphenyl-1,2,4-triazole, 5-amino-3-methyl-1,2,4-triazole, 3-mercaptop-1,2,4-triazole, 1,2,4-triazole-3-carboxylic acid, 1-phenyl-1,2,4-triazole-5-one, 1-phenylurazole, or combinations thereof. Suitable examples of diazoles and thiazole could include 2-mercaptobenzothiazole, 2,5-dimercaptop-1,3,4thiadiazole and derivatives, or combinations thereof. Derivatives of benzotriazole, which are suitable for use in the present invention, include 1-methylbenzotriazole, 5,6-dimethylbenzotriazole, 2-phenylbenzotriazole, 1-hydroxybenzotriazole, methyl 1-benzotriazolcarboxylate, 2-(3,5-dimethyl-2-hydroxyphenyl) benzotriazole, or combinations thereof. In certain embodiments, the amount of azole compound present in the electrodepositable coating composition is ≥0.5 weight % based on the total resin solids of the electrodepositable coating composition. In some embodiments, the amount of azole compound present in the electrodepositable coating composition is ≥0.5 weight % based on the total resin solids of the electrodepositable coating composition. In some embodiments, the amount of azole compound present in the electrodepositable coating composition ranges between any combination of values, which were recited in the preceding sentences, inclusive of the recited values. For example, in some embodiments, the azole compound is present from 2 weight % to 4 weight % based on the total resin solids of the electrodepositable coating composition.

[0023] Alternatively, in some embodiments, in lieu of the application of the electrodepositable coating composition described in the previous paragraph, a color imparting coating composition (described in further detail below) may be applied onto the substrate using techniques known in the art.

[0024] In some embodiments, the method consists essentially of steps (a) through (g) and wherein the materials used in steps (c), (e), and (g) are substantially free of chrome.

Substrate with a Coating System

[0025] The method described above can be used on a variety of substrates. Suitable substrates that can be used with the
present invention include metal substrates, metal alloy substrates, and/or substrates that have been metallized, such as nickel plated plastic. In some embodiments, the metal or metal alloy can be steel and/or aluminum. For example, the steel substrate could be cold rolled steel, electrogalvannealed steel, and/or hot dipped galvanized steel. Aluminum alloys of the 2XXX, 5XXX, 6XXX, or 7XXX series as well as clad aluminum alloys may also be used as the substrate. The substrate used in the present invention may also comprise titanium and/or titanium alloys. In some embodiments, the substrate may comprise a portion of a vehicle such as a vehicular body (e.g., without limitation, door, body panel, trunk deck lid, roof panel, hood, roof and/or stringers, rivets, landing gear components, and/or skins used on an aircraft) and/or a vehicular frame. As used herein, “vehicle” or variations thereof includes, but is not limited to, civilian, commercial and military aircraft, and/or land vehicles such as cars, motorcycles, and/or trucks.

The various coating compositions described herein may be applied as part of a coating system that can be deposited onto the substrate. The coating system is typically comprised of a number of coating layers. A coating layer is usually formed when a coating composition (e.g., primer-surfacer, color imparting, and/or substantially clear coating composition; described further below) that is deposited onto the substrate is substantially cured or dried by methods known in the art (e.g., by thermal heating).

Depending on the industry (e.g., aerospace or automotive), various coating layers, such as a primer-surfacer layer or a color imparting coating layer, may be applied onto at least a portion of the electrodepositable coating layer. For example, in the aerospace industry, a color imparting coating layer, such as DESOPHANE (commercially available from PPG Industries, Inc.), is deposited onto at least a portion of the electrodepositable coating layer. In certain embodiments, a primer layer, such as DESOPRIME (commercially available from PPG Industries, Inc.), is disposed between the electrodepositable coating layer and the color imparting coating layer.

In a conventional coating system used in the automotive industry, a primer-surfacer layer, such as DPX-1791, DPX-1804, DSPX-1537, GPXH-5379, OPP-2645, PCC-70118, and 1177-225A (available from PPG Industries, Inc.) is typically deposited onto at least a portion of the electrodepositable coating layer. The primer-surfacer coating layer serves to enhance chip resistance of subsequently applied coating layers (e.g., color imparting coating composition and/or substantially clear coating composition) as well as to aid in the appearance of the subsequently applied layers. As used herein, “primer-surfacer” refers to a primer composition for use under a subsequently applied coating composition, and includes such materials as thermoplastic and/or crosslinking (e.g., thermosetting) film-forming resins generally known in the art of organic coating compositions.

It should be noted that in some embodiments, the primer-surfacer coating layer is not used in the coating system. Therefore, a color imparting coating layer can be deposited onto at least a portion of the electrodepositable coating layer.

In some embodiments, a color imparting coating composition (hereinafter, “basecoat”) is deposited onto at least a portion of the primer surfacer coating layer (if present). Any basecoat coating composition known in the art may be used in the present invention. It should be noted that these basecoat coating compositions typically comprise a colorant.

In certain embodiments, a substantially clear coating composition (hereinafter, “clearcoat”) is deposited onto at least a portion of the basecoat coating layer. As used herein, a “substantially clear” coating layer is substantially transparent and not opaque. In certain embodiments, the substantially clear coating composition can comprise a colorant but not in an amount such as to render the clear coating composition opaque (not substantially transparent) after it has been cured. Any clearcoat coating composition known in the art may be used in the present invention. For example, the clearcoat coating composition that is described in U.S. Pat. Nos. 5,989, 642, 6,245, 855, 6,387, 519, and 7,005, 472 can be used in the coating system. In certain embodiments, the substantially clear coating composition can also comprise a particle, such as a silica particle, that is dispersed in the clearcoat coating composition (such as at the surface of the clearcoat coating composition after curing). In some embodiments, the coating composition comprising the polymer described herein can be used as the clearcoat coating composition.

One or more of the coating compositions described herein can comprise colorants and/or other optional materials, which are known in the art of formulated surface coatings. As used herein, the term “colorant” means any substance that imparts color and/or other opacity and/or other visual effect to the composition. The colorant can be added to the coating in any suitable form, such as discrete particles, dispersions, solutions and/or flakes (e.g., aluminum flakes). A single colorant or a mixture of two or more colorants can be used in the coating composition described herein.

Example colorants include pigments, dyes and tints, such as those used in the paint industry and/or listed in the Dry Color Manufacturers Association (DCMA), as well as special effect compositions. A colorant may include, for example, a finely divided solid powder that is insoluble but wettable under the conditions of use. A colorant can be organic or inorganic and can be agglomerated or non-agglomerated. Colorants can be incorporated into the coatings by use of a grind vehicle, such as an acrylic grind vehicle, the use of which will be familiar to one skilled in the art.

Example pigments and/or pigment compositions include, but are not limited to, carbazole dioxazine cradle pigment, azo, monoozo, disazo, napthalol AS, salt type (lakes), benzimidazolone, condensation, metal complex, isoindolinone, isoindoline and poly cyclic phthalocyanine, quinacridone, perylene, perinone, diketo pyrrolo pyrrole, thioindigo, anthraquinone, indanthrene, anthrapyrimidine, flavanthrone, pyranthrone, anthanthrone, dioxazine, triarylfuranon, quinophthalone pigments, diketo pyrrolo pyrrole red ("DPPBO red"), titanium dioxide, carbon black and mixtures thereof. The terms “pigment” and “colored filler” can be used interchangeably.

Example dyes include, but are not limited to, those that are solvent and/or aqueous based such as phthalocyanine green or blue, iron oxide, bismuth vanadate, anthraquinone, perylene, aluminum and quinacridone.

Example tints include, but are not limited to, pigments dispersed in water-based or water miscible carriers such as AQUA-CHEM 896 commercially available from Degussa, Inc., CHARISMA COLORANTS and MAXTONER INDUSTRIAL COLORANTS commercially available from Accurate Dispersions division of Eastman Chemical, Inc.
As noted above, the colorant can be in the form of a dispersion including, but not limited to, a nanoparticle dispersion. Nanoparticle dispersions can include one or more highly dispersed nanoparticle colorants and/or colorant particles that produce a desired visible color and/or opacity and/or visual effect. Nanoparticle dispersions can include colorants such as pigments or dyes having a particle size of less than 150 nm, such as less than 70 nm, or less than 30 nm. Nanoparticles can be produced by milling stock organic or inorganic pigments with grinding media having a particle size of less than 0.5 mm. Example nanoparticle dispersions and methods for making them are identified in U.S. Pat. No. 6,875,800. Nanoparticle dispersions can also be produced by crystallization, precipitation, gas phase condensation, and chemical attrition (i.e., partial dissolution). In order to minimize re-agglomeration of nanoparticles within the coating, a dispersion of resin-coated nanoparticles can be used. As used herein, a “dispersion of resin-coated nanoparticles” refers to a continuous phase in which is dispersed discreet “composite microparticles” that comprise a nanoparticle and a resin coating on the nanoparticle. Example dispersions of resin-coated nanoparticles and methods for making them are identified in United States Patent Application Publication 2005-0287348, filed Jun. 24, 2004, U.S. Provisional Application No. 60/482,167, filed Jun. 24, 2003, and U.S. patent application Ser. No. 11/337,062, filed Jan. 20, 2006.

Example special effect compositions that may be used include pigments and/or compositions that produce one or more appearance effects such as reflectance, pearlescence, metallic sheen, phosphorescence, fluorescence, photochromism, photosensitivity, thermochromism, goniochromism and/or color-change. Additional special effect compositions can provide other perceptible properties, such as opacity or texture. In a non-limiting embodiment, special effect compositions can produce a color shift, such that the color of the coating changes when the coating is viewed at different angles. Example color effect compositions are identified in U.S. Pat. No. 6,894,086. Additional color effect compositions can include transparent coated mica and/or synthetic mica, coated silica, coated alumina, a transparent liquid crystal pigment, a liquid crystal coating, and/or any composition wherein interference results from a refractive index differential within the material and not because of the refractive index differential between the surface of the material and the air.

In certain non-limiting embodiments, a photosensitive composition and/or photochromic composition, which reversibly alters its color when exposed to one or more light sources, can be used in the coating composition described herein. Photochromic and/or photosensitive compositions can be activated by exposure to radiation of a specified wavelength. When the composition becomes excited, the molecular structure is changed and the altered structure exhibits a new color that is different from the original color of the composition. When the exposure to radiation is removed, the photochromic and/or photosensitive composition can return to a state of rest, in which the original color of the composition returns. In one non-limiting embodiment, the photochromic and/or photosensitive composition can be colorless in a non-excited state and exhibit a color in an excited state. Full color-change can appear within milliseconds to several minutes, such as from 20 seconds to 60 seconds. Example photochromic and/or photosensitive compositions include photochromic dyes.

In a non-limiting embodiment, the photosensitive composition and/or photochromic composition can be associated with and/or at least partially bound to, such as by covalent bonding, a polymer and/or polymeric materials of a polymerizable component. In contrast to some coatings in which the photosensitive composition may migrate out of the coating and crystallize into the substrate, the photosensitive composition and/or photochromic composition associated with and/or at least partially bound to a polymer and/or polymerizable component in accordance with a non-limiting embodiment of the present invention, have minimal migration out of the coating. Example photosensitive compositions and/or photochromic compositions and methods for making them are identified in U.S. application Ser. No. 10/892,919, filed Jul. 16, 2004.

In general, the colorant can be present in any amount sufficient to impart the desired visual and/or color effect. The colorant may comprise from 1 to 65 weight percent of the present compositions, such as from 3 to 40 weight percent or 5 to 35 weight percent, with weight percent based on the total weight of the compositions.

The coating compositions can comprise other optional materials well known in the art of formulated surface coatings, such as plasticizers, anti-oxidants, hindered amine light stabilizers, UV light absorbers and stabilizers, surfactants, flow control agents, thixotropic agents such as bentonite clay, pigments, fillers, organic cosolvents, catalysts, including phosphonic acids and other customary auxiliaries.

It will be further appreciated that one or more of the coating compositions that form the various coating layers described herein can be either “one component” ("1K"), “two component” ("2K"), or even multi-component compositions. A 1K composition will be understood as referring to a composition wherein all of the coating components are maintained in the same container after manufacture, during storage, etc. A 2K composition or multi-component composition will be understood as referring to a composition wherein various components are maintained separately until just prior to application. A 1K or 2K coating composition can be applied to a substrate and cured by any conventional means, such as by heating, forced air, and the like.

The coating compositions that form the various coating layers described herein can be deposited or applied onto the substrate using any technique that is known in the art. For example, the coating compositions can be applied to the substrate by any of a variety of methods including, without limitation, spraying, brushing, dipping, and/or roll coating, among other methods. When a plurality of coating compositions are applied onto a substrate, it should be noted that one coating composition may be applied onto at least a portion of an underlying coating composition either after the underlying coating composition has been cured or prior to the underlying coating composition being cured. If the coating composition is applied onto an underlying coating composition that has not been cured, one or more of the uncured coating compositions may be cured simultaneously.

The coating compositions may be cured using any technique known in the art such as, without limitation, thermal energy, infrared, ionizing or actinic radiation, or by any combination thereof. In certain embodiments, the curing operation can be carried out at temperatures ≥10°C. In other embodiments, the curing operation can be carried out at temperature ≥246°C. In certain embodiments, the curing operation can carried out at temperatures ranging between any
combination of values, which were recited in the preceding sentences, inclusive of the recited values. For example, the curing operation can be carried out at temperatures ranging from 120° C. to 150° C. It should be noted, however, that lower or higher temperatures may be used as necessary to activate the curing mechanisms.

[0046] In certain embodiments, the coating compositions described herein are a low temperature, moisture curable coating compositions. As used herein, the term "low temperature, moisture curable" refers to coating compositions that, following application to a substrate, are capable of curing in the presence of ambient air, the air having a relative humidity of 10% to 100%, such as 25% to 80%, and a temperature in the range of −10° C. to 120° C., such as 5° C. to 80° C., in some cases 10° C. to 60° C. and, in yet other cases, 15° C. to 40° C.

[0047] The dry film thickness of the coating layers described herein can range from 0.1 micron to 500 microns. In other embodiments, the dry film thickness can be ≤125 microns, such as ≤80 microns. For example, the dry film thickness can range from 15 microns to 60 microns.

[0048] While specific embodiments of the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular arrangements disclosed are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the full breadth of the claims appended and any and all equivalents thereof.

EXAMPLES

Example I

[0049] 2024-T3 bare aluminum panels were cleaned by spraying with a solution of CHEMKLEEN 275, an alkaline cleaner available from PPG Industries, for two minutes at 130° F. After alkaline cleaning, the panels were rinsed thoroughly with deionized water. The panels were then immersed in an acidic solution for two minutes at 120° F. The acid solution was prepared by diluting 198.1 grams of 85% phosphoric acid, 8.5 grams of 70% nitric acid, 16.5 grams of TRITON X-100 (available from The Dow Chemical Company) and 11.1 grams of TRITON CF-10 (available from The Dow Chemical Company) to five gallons of volume with deionized water, and then neutralizing to pH 3.0 with CHEMFIL Buffer (available from PPG Industries). After treatment in the acid solution, the panels were rinsed thoroughly with deionized water and blown dry with a warm air blowoff.

[0050] The panels were then electrocoated in an electrodeposition bath (described below) after the bath was subjected to 50% ultrafiltration. The electrodeposition was performed at 100 to 170 volts for 90 seconds at bath temperatures of 24−27° C. After electrodeposition, the panels were all baked at 93° C. (200° F.) for 30 min. in a gas-fired oven. The electrocoated panels were then subjected to ASTM B117 5% neutral salt fog for 3000 hours.

Bath Composition Used in Example I

Resin 1: Phosphated Epoxy Resin Dispersion Preparation

[0051] A mixture of 819.2 parts of bisphenol A diglycidyl ether (EEW 188), 263.5 parts of bisphenol A, and 209.4 parts of 2-n-butoxy-1-ethanol was heated to 115° C. At that point, 0.5 parts of ethyl triphenylphosphonium iodide was added. This mixture was heated and held at a temperature of at least 165° C. for one hour. As the mixture was allowed to cool to 88° C., 51.3 parts of EKTASOLVE EEH solvent and 23.2 parts of 2-n-butoxy-1-ethanol were added. At 88° C., a slurry consisting of 32.1 parts of 85% α-phosphoric acid, 18.9 parts phenylphosphonic acid, and 6.9 parts of EKTASOLVE EEH was added. The reaction mixture was subsequently maintained at a temperature of at least 120° C. for 30 minutes. At that point, the mixture was cooled to 100° C. and 71.5 parts of deionized water was gradually added. Once the water was added, a temperature of about 100° C. was maintained for 2 hours. Then the reaction mixture was cooled to 90° C. and 90.0 parts of diisopropanolamine was added, followed by 413.0 parts of CYMEL 1130 and 3.0 parts of deionized water. After 30 minutes of mixing, 1800.0 parts of this mixture was reverse-thinned into 1506.0 parts of agitation deionized water. An additional 348.0 parts of deionized water was added to yield a homogeneous dispersion which evidenced a solids content of 39.5% after 1 hour at 110° C.

Examples II

[0052] The electrodeposition bath was prepared as follows:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphated epoxy resin dispersion</td>
<td>1522</td>
</tr>
<tr>
<td>Pigment paste¹</td>
<td>331</td>
</tr>
<tr>
<td>Deionized water</td>
<td>1947</td>
</tr>
</tbody>
</table>


[0053] The above ingredients were thoroughly blended to produce a resinous blend having a solids content of 19% with a pigment/binder ratio of 0.2.

Example II

[0054] 2024-T3 bare aluminum panels were cleaned by spraying with a solution of CHEMKLEEN 275, an alkaline cleaner available from PPG Industries, for two minutes at 130° F. After alkaline cleaning, the panels were rinsed thoroughly with deionized water. The panels were then immersed in an acidic solution for two minutes at 120° F. The acid solution was prepared by diluting 198.1 grams of 85% phosphoric acid, 8.5 grams of 70% nitric acid, 16.5 grams of TRITON X-100 (available from The Dow Chemical Company) and 11.1 grams of TRITON CF-10 (available from The Dow Chemical Company) to five gallons of volume with deionized water, and then neutralizing to pH 3.0 with CHEMFIL Buffer (available from PPG Industries). After treatment in the acid solution, the panels were rinsed thoroughly with deionized water. The panels were then immersed in a solution of fluorozirconic acid for two minutes at 100° F. The acid bath was prepared by diluting 16.6 grams of 45% fluorozirconic acid to five gallons of volume with deionized water, and then neutralizing to pH 4.5 with CHEMFIL Buffer (available from PPG Industries). After treatment in the acid solution, the panels were rinsed thoroughly with deionized water and blown dry with a warm air blowoff.

[0055] The panels were then electrocoated in an electrodeposition bath (described below) after the bath was subjected to 50% ultrafiltration. The electrodeposition was performed at 100 to 170 volts for 90 seconds at bath temperatures of 24−27° C. After electrodeposition, the panels were all baked at 93° C. (200° F.) for 30 min. in a gas-fired oven. The
electrocoated panels were then subjected to ASTM B117 5% neutral salt fog for 3000 hours.

Bath Composition Used in Example II

Resin II: Phosphated Epoxy Resin Dispersion Preparation

A mixture of 819.2 parts of bisphenol A diglycidyl ether (EEW 188), 263.5 parts of bisphenol A, and 209.4 parts of 2-n-butoxy-1-ethanol was heated to 115° C. At that point, 0.8 parts of ethyl triphenylphosphonium iodide was added. This mixture was heated and held at a temperature of at least 165° C. for one hour. As the mixture was allowed to cool to 88° C., 51.3 parts of EKTASOLVE EEH solvent and 23.2 parts of 2-n-butoxy-1-ethanol were added. At 88° C., a slurry consisting of 32.1 parts of 85% o-phosphoric acid, 18.9 parts phenylphosphonic acid, and 6.9 parts of EKTASOLVE EEH was added. The reaction mixture was subsequently maintained at a temperature of at least 120° C. for 30 minutes. At that point, the mixture was cooled to 100° C. and 71.5 parts of deionized water was gradually added. Once the water was added, a temperature of about 100° C. was maintained for 2 hours. Then the reaction mixture was cooled to 90° C. and 90.0 parts of disopropylamine was added, followed by 413.0 parts of CYMEL 1130 and 3.0 parts of deionized water. After 30 minutes of mixing, 1800.0 parts of this mixture was reverse-thinned into 1506.0 parts of agitated deionized water. An additional 348.0 parts of deionized water was added to yield a homogenous dispersion which evidenced a solids content of 39.5% after 1 hour at 110° C.

A resinous blend of the above-described phosphated epoxy resin was prepared as follows:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphated epoxy resin dispersion of Example I + corrosion inhibitor</td>
<td>1522</td>
</tr>
<tr>
<td>Pigment paste</td>
<td>331</td>
</tr>
<tr>
<td>Deionized water</td>
<td>1947</td>
</tr>
</tbody>
</table>

The above ingredients were thoroughly blended to produce a resinous blend having a solids content of 19% with a pigment/binder ratio of 0.2.

Test Result Summary

Test results indicated that the panels from Example II exhibited improved corrosion performance (i.e. less blistering; face and scribe), less corrosion in the scribe, and less pitting when compared to panels from Example I.

What is claimed is:

1. A method for coating a substrate comprising: (a) applying a caustic cleaner onto at least a portion of the substrate; (b) rinsing at least a portion of the substrate that was subjected to step (a) with water; (c) applying an acid cleaner onto at least a portion of the caustically cleaned substrate; (d) rinsing at least a portion of the substrate that was subjected to step (c) with water; and (e) depositing a conversion coating composition comprising zincium onto at least a portion of the acid cleaned substrate; and wherein at least one of the materials used in steps (c) and (e) is substantially chrome free.

2. The method according to claim 1, wherein the method further comprises (f) rinsing at least a portion of the substrate that was subjected to step (e) with water; and (g) depositing an electrodepositable coating composition onto at least a portion of the conversion coating, wherein the electrodepositable coating composition comprises a corrosion inhibitor.

3. The method according to claim 2, wherein the electrodepositable coating composition is substantially free of chrome.

4. The method according to claim 2, wherein the corrosion inhibitor comprises an azole compound.

5. The method according to claim 4, wherein the azole compound comprises benzothisazole, 3-mercapto-1,2,4-triazole, 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 1-methylbenzotriazole, or combinations thereof.

6. The method according to claim 2, wherein the electrodepositable coating composition comprises an ungelled phosphated epoxy resin in which the phosphated epoxy resin comprises a mixture of the reaction product of a polymeric epoxy compound with phosphoric acid, an organophosphonic acid, an organophosphinic acid, or combinations thereof.

7. The method according to claim 1, wherein the acid cleaner comprises phosphoric acid, sulfonic acid, hydrofluoric acid, nitric acid, or combinations thereof.

8. The method according to claim 1, wherein the conversion coating composition is substantially free of chrome.

9. A method for coating a substrate comprising: (a) applying a caustic cleaner onto at least a portion of the substrate; (b) rinsing at least a portion of the substrate that was subjected to step (a) with water; (c) applying an acid cleaner onto at least a portion of the caustically cleaned substrate; (d) rinsing at least a portion of the substrate that was subjected to step (c) with water; and (e) depositing a conversion coating composition comprising zincium onto at least a portion of the acid cleaned substrate; and wherein the materials used in steps (c) and (e) are substantially chrome free.

10. The method according to claim 9, wherein the method further comprises (f) rinsing at least a portion of the substrate that was subjected to step (e) with water; and (g) depositing an electrodepositable coating composition onto at least a portion of the conversion coating composition, wherein the electrodepositable coating composition comprises a corrosion inhibitor.

11. The method according to claim 10, wherein the corrosion inhibitor comprises an azole compound.

12. The method according to claim 11, wherein the azole compound comprises benzothisazole, 3-mercapto-1,2,4-triazole, 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 1-methylbenzotriazole, or combinations thereof.

13. The method according to claim 10, wherein the electrodepositable coating composition comprises an ungelled phosphated epoxy resin in which the phosphated epoxy resin comprises the reaction product of a polymeric epoxy compound with phosphoric acid, an organophosphonic acid, an organophosphinic acid, or combinations thereof.

14. The method according to claim 9, wherein the materials used in steps (c) and (e) are substantially chrome free.

15. A method for coating a substrate consisting essentially of: (a) applying a caustic cleaner onto at least a portion of the substrate; (b) rinsing at least a portion of the substrate that was subjected to step (a) with water; (c) applying an acid cleaner onto at least a portion of the caustically cleaned substrate; (d) rinsing at least a portion of the substrate that was subjected to step (c) with water; (e) depositing a conversion coating composition comprising zincium onto at least a portion of the acid cleaned substrate; (f) rinsing at least a portion of the substrate that was subjected to step (e) with water; and (g) depositing an electrodepositable coating composition onto at least a portion of the conversion coating, wherein the electrodepositable coating composition comprises a corrosion inhibitor.
least a portion of the conversion coating composition, wherein the electrodepositable coating composition comprises a corrosion inhibitor; and wherein the materials used in steps (c), (e), and (g) are substantially free of chrome.

16. The method according to claim 15, wherein the corrosion inhibitor comprises an azole compound.

17. The method according to claim 16, wherein the azole compound comprises benzotriazole, 3-mercapto-1,2,4-triazole, 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4thiadiazole, 1-methylbenzotriazole, or combinations thereof.

18. The method according to claim 15, wherein the electrodepositable coating composition comprises an ungelled phosphated epoxy resin in which the phosphated epoxy resin comprises a mixture of the reaction product of a polymeric epoxy compound with phosphoric acid, an organophosphonic acid, an organophosphinic acid, or combinations thereof.

19. A substrate coated according to claim 1.

20. The substrate according to claim 19, wherein the substrate is aluminum.

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