ACID CLEANERS FOR METAL SUBSTRATES AND ASSOCIATED METHODS FOR CLEANING AND COATING METAL SUBSTRATES

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Abstract

Disclosed are methods for cleaning and coating metal substrates, and the coated substrate formed therein, that include contacting the substrate with an acid and then contacting the cleaned substrate with an electrodepositable coating composition comprising a film forming polymer and a corrosion inhibitor.
ACID CLEANERS FOR METAL SUBSTRATES AND ASSOCIATED METHODS FOR CLEANING AND COATING METAL SUBSTRATES

FIELD OF THE INVENTION

[0001] The present invention relates to acid cleaners for metal substrates and associated methods for cleaning metal substrates with the acid cleaners prior to application of a pretreatment composition and/or an electrodepositable coating composition.

BACKGROUND INFORMATION

[0002] The use of protective coatings on metal substrates for improved corrosion resistance and paint adhesion is common. Conventional techniques for coating such substrates include techniques that involve pretreating the metal substrate with a pretreatment composition and/or with an electrodepositable coating composition.

SUMMARY OF THE INVENTION

[0003] In certain embodiments, the present invention is directed to a method comprising: (a) contacting a substrate with an acid; and then (b) contacting the substrate with an electrodepositable coating composition comprising (i) a film-forming polymer; and (ii) a corrosion inhibitor; with the proviso that the method does not comprise contacting the substrate with a pretreatment composition prior to step (b).

DETAILED DESCRIPTION OF THE INVENTION

[0004] For purposes of the following detailed description, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term “about”. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0005] Notwithstanding that the numerical ranges and parameters set forth in the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[0006] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of “1 to 10” is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

[0007] In this application, the use of the singular includes the plural and plural encompasses singular, unless specifically stated otherwise. In addition, in this application, the use of “or” means “and/or” unless specifically stated otherwise, even though “and/or” may be explicitly used in certain instances.

[0008] Certain embodiments of the present invention are directed to methods for cleaning a substrate by contacting the metal substrate with an acid.

[0009] The acid cleaned substrate, in certain embodiments, may then be contacted with a pretreatment composition. In certain of these embodiments, the pretreatment composition includes a group IIIB and/or IVB metal compound, wherein the citric acid cleaner acts to provide increased deposition of the group IIIB and/or IVB metal onto the metal substrate surface, wherein the increased metal content acts to improve corrosion resistance.

[0010] In certain other embodiments, a film forming composition, such as an electrodepositable coating composition, may be applied over the acid cleaned and optionally pretreated substrate. In these embodiments, the acid provides improved corrosion protection to the coated substrate as compared with coated and uncleared substrates or substrates cleaned with alkaline cleaners and coated as described above.

[0011] In certain other embodiments, a film forming composition, such as an electrodepositable coating composition, may be applied over the acid cleaned substrate without first contacting the substrate with a pretreatment composition. In certain of these embodiments, the acid acts to improve corrosion resistance of these acid cleaned and electrocoated substrates as compared with coated and uncleared substrates or substrates cleaned with alkaline cleaners and electrocoated as described above.

[0012] Each of these embodiments is described below:

Substrate

[0013] Suitable substrates that can be cleaned and coated in accordance with the present invention include, without limitation, metal substrates, metal alloy substrates, and/or substrates that have been metalized, such as nickel plated plastic. In some embodiments, the metal or metal alloy can be aluminum and/or steel. For example, the steel substrate could be cold rolled steel, electrogallvanized steel, and hot dipped galvanized steel. Moreover, 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, and/or roof) and/or a vehicular frame. As used herein, “vehicle” or variations thereof includes, but is not limited to, civilian, commercial, and military land vehicles such as cars, motorcycles, and trucks.

Cleaning

[0014] In certain embodiments, the substrates may be contacted with an acid prior to contacting the substrate with a pretreatment composition and/or an electrodepositable coating composition.

[0015] While not wanting to be bound by any theory, it is believed that the acid etches the substrate to provide increased surface area to the substrate. Increased surface area is believed to provide improved adhesion between the substrate and the subsequently applied coating materials, which is believed to improve corrosion resistance to the coated panels. In addition, increased etching of the substrate material is
believed to allow for increased deposition of metal from the pretreatment composition, when utilized, which also is believed to increase corrosion resistance to the coated panels. Further, increased etching of the substrate material is believed for increased deposition of metal from the electrodepositable coating composition, when utilized, at the interface between the electrodipositable coating composition and the substrate, which may provide even more corrosion resistance to the coated panels.

In certain embodiments, the acid comprises a single acid, while in other embodiments the acid comprises a mixture of acids.

In certain embodiments, the acid comprises a weak acid, while in other embodiments the acid comprises a strong acid. A weak acid, by definition, is an acid that dissociates incompletely (i.e. it does not release all its hydrogens in solution), while a strong acid is an acid that ionizes completely in an aqueous solution (i.e. which release all of their hydrogen atoms when dissolved in water).

In still other embodiments, the acid comprises an organic acid. An organic compound, by definition, is an organic compound having acidic properties. Exemplary organic acids include uric acid, sulfonic acid, and carboxylic acids including lactic acid, formic acid, citric acid, and oxalic acid, as well as mixtures thereof.

In still other embodiments, the acid comprises a mineral acid. A mineral acid, by definition, is an acid derived from an inorganic compound. Exemplary mineral acids include hydrochloric acid, sulfuric acid, boric acid, phosphoric acid, hydrofluoric acid, hydrobromic acid, nitric acid, and mixtures thereof.

In still other embodiments, the acid may comprise any combination of one or more organic acids and/or mineral acids.

In certain of these embodiments, the carboxylic acid selected for use in the compositions described herein has a water solubility of 1 g/L at 20°C. Carboxylic acids suitable for use include, for example, monocarboxylic acids, such as formic acid, acetic acid, propionic acid, methylacetic acid, butyric acid, ethylacetic acid, n-valeric acid, n-butanecarboxylic acid, acrylic acid, propionic acid, methacrylic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid; dicarboxylic acids, such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, maleic acid, and fumaric acid; aliphatic hydroxy acids, such as glycolic acid, lactic acid, tartaric acid, glyceric acid, malic acid, tartaric acid, citramalic acid, citric acid, isocitric acid, leucine acid, mevalonic acid, pantothenic acid, ricinoleic acid, cerylalcoholic acid, quinic acid, and sikhimic acid; aromatic hydroxy acids, such as salicylic acid, cressoate acid, vanillie acid, syringic acid, pyrocatechitic acid, resorcylic acid, protocatechitic acid, gentisic acid, orsellinic acid, gallic acid, mandelic acid, benzolic acid, atracitivity acid, mellitolic acid, phloreotic acid, coumaric acid, umbellenic acid, caffeic acid, ferulic acid, and sinapic acid. Mixtures of any of the foregoing may also be used.

In certain embodiments, the acid is incorporated into an acid cleaner that also may include other components such as water, surfactants and/or buffers, including commercially available surfactants and/or buffers.

In certain other embodiments, the substrate to be treated in accordance with the methods of the present invention may first be cleaned to remove grease, dirt, or other extraneous matter. This is often done by employing mild or strong alkaline cleaners, such as are commercially available and conventionally used in metal pretreatment processes. Examples of alkaline cleaners suitable for use in the present invention include Chemikleen 163, Chemikleen 177, Chemikleen 201L P and Chemikleen 490MX, each of which are commercially available from PPG Industries, Inc. In certain embodiments, a surfactant may also be included in the alkaline cleaner, such as 181L P commercially available from PPG Industries, Inc. Such cleaners are often followed and/or preceded by a water rinse. After cleaning, the bare substrate materials may be rinsed thoroughly with deionized water.

In certain of these embodiments, the alkaline cleaner is applied to the substrate prior to the acid cleaner, while in other embodiments the acid cleaner is applied to the substrate prior to the alkaline cleaner.

**Pretreatment**

In certain embodiments of the methods of the present invention, after the substrate is contacted with the acid, it may then be contacted with a pretreatment composition. As used herein, the term “pretreatment composition” refers to a composition that upon contact with a substrate reacts with and chemically alters the substrate surface and binds to it to form a protective layer.

In certain other embodiments of the present invention, the pretreatment composition comprises a group IIIB and/or IVB metal compound.

In certain embodiments, the pretreatment composition comprises a carrier, often an aqueous medium, so that the composition is in the form of a solution or dispersion of a group IIIB or IVB metal compound in the carrier. In these embodiments, the solution or dispersion may be brought into contact with the substrate by any of a variety of known techniques, such as dipping or immersion, spraying, intermittent spraying, dipping followed by spraying, spraying followed by dipping, brushing, or roll-coating. In certain embodiments, the solution or dispersion when applied to the metal substrate is at a temperature ranging from 60 to 150°F. (15 to 65°C). The contact time is often from 10 seconds to five minutes, such as 30 seconds to 2 minutes.

As used herein, the term “group IIIB and/or IVB metal” refers to an element that is in group IIIB or group IVB of the CAS Periodic Table of the Elements as is shown, for example, in the Handbook of Chemistry and Physics, 63rd edition (1983). Where applicable, the metal itself may be used. In certain embodiments, a group IIIB and/or IVB metal compound is used. As used herein, the term “group IIIB and/or IVB metal compound” refers to compounds that include at least one element that is in group IIIB or group IVB of the CAS Periodic Table of the Elements.

In certain embodiments, the group IIIIB and/or IVB metal compound used in the pretreatment composition is a compound of zirconium, titanium, hafnium, yttrium, cerium, or a mixture thereof. Suitable compounds of zirconium include, but are not limited to, hexafluorozirconic acid, alkali metal and ammonium salts thereof, ammonium zirconium carbonate, zirconyl nitrate, zirconium carboxylates and zirconium hydroxy carboxylates, such as hydrofluorozirconic acid, zirconium acetate, zirconium oxalate, ammonium zirconium glycolate, ammonium zirconium lactate, ammonium zirconium citrate, and mixtures thereof. Suitable compounds of titanium include, but are not limited to, fluorotitanic acid and its salts. A suitable compound of hafnium includes, but is
not limited to, hafnium nitrate. A suitable compound of yttrium includes, but is not limited to, yttrium nitrate. A suitable compound of cerium includes, but is not limited to, cerous nitrate.

[0030] In certain embodiments, the group TIM and/or IVB metal compound is present in the pretreatment composition in an amount of at least 10 ppm metal, such as at least 100 ppm metal, or, in some cases, at least 150 ppm metal. In certain embodiments, the group IIIIB and/or IVB metal compound is present in the pretreatment composition in an amount of no more than 5000 ppm metal, such as no more than 300 ppm metal, or, in some cases, no more than 250 ppm metal. The amount of group IIIIB and/or IVB metal in the pretreatment composition can range between any combination of the recited values inclusive of the recited values. The pH of the pretreatment composition often ranges from 2.0 to 7.0, such as 3.5 to 5.5. The pH of the pretreatment composition may be adjusted using, for example, any of the acids and bases identified earlier with respect to cleaning the substrate.

[0031] In some embodiments, the pretreatment composition may be a silane or a non-crystalline phosphate, such as iron phosphate, containing pretreatment composition. Suitable silane containing pretreatment compositions include, but are not limited to, certain commercially available products, such as Silquest A-1100 Silane, which is described in the Examples herein and which is commercially available from Momentive Performance Materials. Suitable non-crystalline phosphate containing pretreatment composition include pretreatment composition that comprise, iron phosphate, manganese phosphate, calcium phosphate, magnesium phosphate, cobalt phosphate, or an organophosphate and/or organophosphonate, such as is disclosed in U.S. Pat. No. 5,294,265 at col. 1, line 53 to col. 3, line 12 and 5,306,526 at col. 1, line 46 to col. 3, line 8, the cited portions of which being incorporated herein by reference. Suitable non-crystalline phosphate containing pretreatment compositions are commercially available, such as Chemfos® 158 and Chemfos® 51, which are iron phosphate pretreatment compositions commercially available from PPG Industries, Inc.

[0032] In certain embodiments, the pretreatment composition also comprises an electropositive metal, such as copper. The source of electropositive metal, such as copper, in the pretreatment composition may comprise, for example, any of the materials described earlier with respect to the plating solution. In certain embodiments, the electropositive metal is included in such pretreatment compositions in an amount of at least 1 ppm, such as at least 5 ppm, or in some cases, at least 10 ppm of total metal (measured as elemental metal). In certain embodiments, the electropositive metal is included in such pretreatment compositions in an amount of no more than 500 ppm, such as no more than 100 ppm, or in some cases, no more than 50 ppm of total metal (measured as elemental metal).

[0033] In certain embodiments, the pretreatment composition comprises a resinous binder. Suitable resins include reaction products of one or more alkanolamines and an epoxy-functional material containing at least two epoxy groups, such as those disclosed in U.S. Pat. No. 5,653,825. In some cases, such resins contain beta hydroxy ester, imide, or sulfide functionality, incorporated by using dimethylolpropionic acid, phthalimide, or mercapto glycerine as an additional reactant in the preparation of the resin. Alternatively, the reaction product is that of the diglycidyl ether of Bisphenol A (commercially available from Shell Chemical Company as EPON 880), dimethylol propionic acid, and diethanolamine in a 0.6 to 5.0:0.05 to 5.5:1 mole ratio. Other suitable resinous binders include water soluble and water dispersible polyacrylic acids as disclosed in U.S. Pat. Nos. 3,912,548 and 5,328,525; phenol formaldehyde resins as described in U.S. Pat. No. 5,662,746; water soluble polyamides such as those disclosed in WO 95/38369; copolymers of maleic or acrylic acid with allyl ether as described in Canadian Patent application 2,087,352; and water soluble and dispersible resins including epoxy resins, aminoplasts, phenol-formaldehyde resins, tannins, and polylvinylenplas as discussed in U.S. Pat. No. 5,449,415.

[0034] In these embodiments of the present invention, the resinous binder is present in the pretreatment composition in an amount of 0.005 percent to 30 percent by weight, such as 0.5 to 3 percent by weight, based on the total weight of the ingredients in the composition.

[0035] In other embodiments, however, the pretreatment composition is substantially free or, in some cases, completely free of any resinous binder. As used herein, the term “substantially free”, when used with reference to the absence of resinous binder in the pretreatment composition, means that any resinous binder is present in the pretreatment composition in an amount of less than 0.005 percent by weight. As used herein, the term “completely free” means that there is no resinous binder in the pretreatment composition at all.

[0036] The pretreatment composition may optionally contain other materials, such as nonionic surfactants and auxiliaries conventionally used in the art of pretreatment. In an aqueous medium, water dispersible organic solvents, for example, alcohols with up to about 8 carbon atoms, such as methanol, isopropanol, and the like, may be present; or glycol ethers such as the monoalkyl ethers of ethylene glycol, diethylene glycol, or propylene glycol, and the like. When present, water dispersible organic solvents are typically used in amounts up to about ten percent by volume, based on the total volume of aqueous medium.

[0037] Other optional materials include surfactants that function as defoamers or substrate wetting agents, such as those materials and amounts described earlier with respect to the plating solution.

[0038] In certain embodiments, the pretreatment composition also comprises a reaction accelerator, such as nitrite ions, nitro-group containing compounds, hydroxylamine sulfate, persulfate ions, sulfite ions, hyposulfite ions, peroxides, iron (III) ions, citric acid iron compounds, bromate ions, perchlorinate ions, chlorate ions, chloride ions as well as ascorbic acid, citric acid, tartaric acid, malonic acid, succinic acid and salts thereof. Specific examples of suitable materials and their amounts are described in United States Patent Application Publication No. 2004/0163736 A1 at [0032] to [0041], the cited portion of which being incorporated herein by reference.

[0039] In certain embodiments, the pretreatment composition also comprises a filler, such as a siliceous filler. Non-limiting examples of suitable fillers include silica, mica, montmorillonite, kaolinite, asbestos, talc, diatomaceous earth, vermiculite, natural and synthetic zeolites, cement, calcium silicate, aluminum silicate, sodium aluminum silicate, aluminum polysilicate, alumina silica gels, and glass particles. In addition to the siliceous fillers other finely divided particulate substantially water-insoluble fillers may also be employed. Examples of such optional fillers include carbon black, charcoal, graphite, titanium oxide, iron oxide,
copper oxide, zinc oxide, antimony oxide, zirconia, magnesium alumina, molybdenum disulfide, zinc sulfide, barium sulfate, strontium sulfate, calcium carbonate, and magnesium carbonate.

As indicated, in certain embodiments, the pretreatment composition is substantially or, in some cases, completely free of chromate and/or heavy metal phosphate. As used herein, the term "substantially free" when used in reference to the absence of chromate and/or heavy metal phosphate, such as zinc phosphate, in the pretreatment composition means that these substances are not present in the composition to such an extent that they cause a burden on the environment. That is, they are not substantially used and the formation of sludge, such as zinc phosphate, formed in the case of using a treating agent based on zinc phosphate, is eliminated.

Moreover, in certain embodiments, the pretreatment composition is substantially free, or, in some cases, completely free of any organic materials. As used herein, the term "substantially free", when used with reference to the absence of organic materials in the composition, means that any organic materials are present in the composition, if at all, as an incidental impurity. In other words, the presence of any organic material does not affect the properties of the composition. As used herein, the term "completely free" means that there is no organic material in the composition at all.

In certain embodiments, the film coverage of the residue of the pretreatment coating composition generally ranges from 1 to 1000 milligrams per square meter (mg/m²), such as 10 to 400 mg/m². The thickness of the pretreatment coating can vary, but is generally very thin, often having a thickness of less than 1 micrometer, in some cases it is from 1 to 500 nanometers, and, in yet other cases, it is 10 to 300 nanometers.

In certain other embodiments of the present invention, the pretreatment composition comprises (a) a rare earth metal; and (b) a zirconyl compound. These pretreatment compositions are applied directly to the metal substrate without the prior application of an electropositive metal (i.e., in a one-step pretreatment process).

Often, the pretreatment composition comprises a carrier, often an aqueous medium, so that the composition is in the form of a solution or dispersion of the rare earth metal compound and/or other pretreatment composition components in the carrier. In these embodiments, the solution or dispersion may be brought into contact with the substrate by any of a variety of known techniques, such as dipping or immersion, spraying, intermittent spraying, dipping followed by spraying, spraying followed by dipping, brushing, or roll-coating. In certain embodiments, the solution or dispersion when applied to the metal substrate is at a temperature ranging from 60 to 150°C ( 15 to 65°C). The contact time is often from 10 seconds to five minutes, such as 30 seconds to 2 minutes.

As defined by IUPAC and used herein, rare earth elements or rare earth metals are a collection of seventeen chemical elements in the periodic table, specifically the fifteen lanthanoids (the fifteen elements with atomic numbers 57 through 71, from lanthanum to lutetium) plus scandium and yttrium. Where applicable, the metal themselves may be used. In certain embodiments, a rare earth metal compound is used. As used herein, the term "rare earth metal compound" refers to compounds that include at least one element that is a rare earth element as defined above.

In certain embodiments, the rare earth metal compound used in the pretreatment composition is a compound of yttrium, cerium, praseodymium, or a mixture thereof. Exemplary compounds that may be used include praseodymium chloride, praseodymium nitrate, cerium sulfate, cerium chloride, cerium nitrate, cerium sulfate, yttrium chloride, yttrium nitrate, yttrium sulfate.

In certain embodiments, the rare earth metal compound is present in the pretreatment composition in an amount of at least 10 ppm metal, such as at least 100 ppm metal, or, in some cases, at least 150 ppm metal. In certain embodiments, the rare earth metal compound is present in the pretreatment composition in an amount of no more than 5000 ppm metal, such as no more than 300 ppm metal, or, in some cases, no more than 250 ppm metal. The amount of rare earth metal in the pretreatment composition can range between any of the recited values inclusive of the recited values.

As noted above, the pretreatment composition also comprises a zirconyl compound. A zirconyl compound, as defined herein, refers to a zirconium compound with an oxide or a hydroxide group on a zirconium atom.

In certain embodiments, the zirconyl compound in the pretreatment composition is zirconyl nitrate (ZrO(NO₃)₂), zirconyl acetate, zirconyl carbonate, zirconyl sulfate, or a mixture thereof.

In certain embodiments, the ratio of zirconium (from the zirconyl compound or compounds) to rare earth metal (from the rare earth metal or rare earth metal compound) is between 200/1 and 1/1. In other embodiments, the ratio is between 100/1 and 2/1. In certain embodiments, the ratio is 20/1.

In certain embodiments, the pretreatment composition also includes a group IIIb, group IVb, and/or group VB metal. As used herein, the term "group IIIb, group IVb, and/or group VB metal" refers to an element that is in group IIIb or group IVb or group VB of the CAS Periodic Table of Elements as is shown, for example, in the Handbook of Chemistry and Physics, 63rd edition (1983). Where applicable, the metal themselves may be used. In certain embodiments, a group IIIb, group IV and/or a group VB metal compound is used. As used herein, the term "a group IIIb, group IV and/or a group VB metal compound" refers to compounds that include at least one element that is in the group IIIb or group IVb or group VB of the CAS Periodic Table of Elements.

In certain embodiments, the group IIIb or group IVb or group VB metal compound used in the pretreatment composition is a compound of zirconium, titanium, hafnium, yttrium, cerium, praseodymium, or a mixture thereof. Suitable compounds of zirconium include, but are not limited to, hexahydrouroric acid, alkali metal and ammonium salts thereof, ammonium zirconium carbonate, zirconyl nitrate, zirconium carboxylates and zirconium hydroxy carboxylates, such as hydroxylzirconic acid, zirconium acetate, zirconium oxalate, ammonium zirconium glycolate, ammonium zirconium lactate, ammonium zirconium citrate, and mixtures thereof. Suitable compounds of titanium include, but are not limited to, fluorotitanic acid and its salts. A suitable compound of hafnium includes, but is not limited to, hafnium nitrate. A suitable compound of yttrium includes, but is not limited to, yttrium nitrate. A suitable compound of cerium includes, but is not limited to, cerous nitrate.
In certain embodiments, the group IIIB or group IVB metal compound is present in the pretreatment composition in an amount of at least 10 ppm metal, such as at least 100 ppm metal, and in some cases, at least 150 ppm metal. In certain embodiments, the group IIIB or group IVB or group VB metal compound is present in the pretreatment composition in an amount of no more than 5000 ppm metal, such as no more than 300 ppm metal, and in some cases, no more than 250 ppm metal. The amount of group IIIB or group IVB or group VB metal in the pretreatment composition can range between any combination of the recited values inclusive of the recited values.

In certain embodiments, the pretreatment composition also comprises an electropositive metal. As used herein, the term “electropositive metal” refers to metals that are more electropositive than the metal substrate. This means that, for purposes of the present invention, the term “electropositive metal” encompasses metals that are less easily oxidized than the metal of the metal substrate. As will be appreciated by those skilled in the art, the tendency of a metal to be oxidized is called the oxidation potential, is expressed in volts, and is measured relative to a standard hydrogen electrode, which is arbitrarily assigned an oxidation potential of zero. The oxidation potential for several elements is set forth in the table below. An element is less easily oxidized than another element if it has a voltage value, E*, in the following table, that is greater than the element to which it is being compared.

<table>
<thead>
<tr>
<th>Element</th>
<th>Half-cell reaction</th>
<th>Voltage, E*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>K⁺ + e⁻ → K⁻</td>
<td>-2.93</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca⁺⁺ + 2e⁻ → Ca⁻</td>
<td>-2.87</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na⁺ + e⁻ → Na⁻</td>
<td>-2.71</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg⁺⁺ + 2e⁻ → Mg⁻</td>
<td>-2.37</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al⁺⁺⁺ + 3e⁻ → Al⁻</td>
<td>-1.66</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn⁺⁺ + 2e⁻ → Zn⁻</td>
<td>-0.76</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe⁺⁺ + 2e⁻ → Fe⁻</td>
<td>-0.44</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni⁺⁺ + 2e⁻ → Ni⁻</td>
<td>-0.25</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn⁺⁺ + 2e⁻ → Sn⁻</td>
<td>-0.14</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb⁺⁺ + 2e⁻ → Pb⁻</td>
<td>-0.13</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2H⁺ + 2e⁻ → H₂</td>
<td>-0.00</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu⁺⁺ + 2e⁻ → Cu⁻</td>
<td>0.34</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg⁺⁺ + 2e⁻ → 2Hg⁻</td>
<td>0.79</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag⁺ + e⁻ → Ag⁻</td>
<td>0.80</td>
</tr>
<tr>
<td>Gold</td>
<td>Au⁺⁺⁺ + 3e⁻ → Au⁻</td>
<td>1.50</td>
</tr>
</tbody>
</table>

In certain embodiments, the electropositive metal is used in the pretreatment composition in a water soluble metal salt. In certain embodiments of the present invention, the water soluble metal salt is a water soluble copper compound. Specific examples of water soluble copper compounds, which are suitable for use in the present invention include, but are not limited to, copper cyanide, copper potassium cyanide, copper sulfate, copper nitrate, copper pyrophosphate, copper thiocyanate, disodium copper ethylenediaminetetraacetate tetrahydrate, copper bromide, copper oxide, copper hydroxide, copper chloride, copper fluoride, copper gluconate, copper citrate, copper lauryl sarcosinate, copper formate, copper acetate, copper propionate, copper butyrate, copper lactate, copper oxalate, copper phytate, copper tartarate, copper malate, copper succinate, copper malonate, copper maleate, copper benzoate, copper salicylate, copper aspartate, copper glutamate, copper fumarate, copper glycerophosphate, sodium copper chlorophyllin, copper fluorosilicate, copper fluoroborate and copper iodate, as well as copper salts of carboxylic acids in the homologous series formic acid to decanoic acid, copper salts of polybasic acids in the series oxalic acid to suberic acid, and copper salts of hydroxyacarboxylic acids, including glycolic, lactic, tartaric, malic and citric acids.

When copper ions supplied from such a water-soluble copper compound are precipitated as an impurity in the form of copper sulfate, copper oxide, etc., it may be preferable to add a complexing agent that suppresses the precipitation of copper ions, thus stabilizing them as a copper complex in the solution.

In certain embodiments, the copper compound is added as a copper complex salt such as K₂[Cu(CN)₄] or Cu-EDTA, which can be present stably in the composition on its own, but it is also possible to form a copper complex that can be present stably in the composition by combining a complexing agent with a compound that is difficultly soluble on its own. Examples thereof include a copper cyanide complex formed by a combination of CuCN and KCN or a combination of CuSCN and KSCN or KCN, and a Cu-EDTA complex formed by a combination of CuSO₄ and EDTA-2Na.

With regard to the complexing agent, a compound that can form a complex with copper ions can be used; examples thereof include inorganic compounds, such as cyanide compounds and thiocyanate compounds, and polycarboxylic acids, and specific examples thereof include ethylenediaminetetraacetic acid, salts of ethylenediaminetetraacetic acid, such as dihydrogen disodium ethylenediaminetetraacetate dihydride, aminocarboxylic acids, such as nitrilotriacetic acid and iminodiacetic acid, oxyacarboxylic acids, such as citric acid and tartaric acid, succinic acid, oxalic acid, ethylenediaminetetraacetic acid, and glycine.

In certain embodiments, the electropositive metal, such as copper, is included in the pretreatment compositions in an amount of at least 1 ppm, such as at least 5 ppm, or in some cases, at least 10 ppm of total metal (measured as elemental metal). In certain embodiments, the electropositive metal is included in such pretreatment compositions in an amount of no more than 500 ppm, such as no more than 100 ppm, or in some cases, no more than 50 ppm of total metal (measured as elemental metal). The amount of electropositive metal in the pretreatment composition can range between any combination of the recited values inclusive of the recited values.

The pretreatment composition may optionally contain other materials, such as nonionic surfactants and auxiliaries conventionally used in the art of pretreatment. In an aqueous medium, water dispersible organic solvents, for example, alcohols with up to about 8 carbon atoms, such as methanol, isopropanol, and the like, may be present; or glycol ethers such as the monoalkyl ethers of ethylene glycol, diethylene glycol, or propylene glycol, and the like. When present,
water dispersible organic solvents are typically used in amounts up to about ten percent by volume, based on the total volume of aqueous medium.

[0062] Other optional materials include surfactants that function as defoamers or substrate wetting agents, such as those materials and amounts described earlier with respect to the plating solution.

[0063] In certain embodiments, the pretreatment composition also comprises a reaction accelerator, such as nitrite ions, nitro-group containing compounds, hydroxylamine sulfate, persulfate ions, sulfite ions, hyposulfite ions, peroxides, iron (III) ions, citric acid iron compounds, bromate ions, perchlorate ions, chloride ions, chlorite ions as well as ascorbic acid, citric acid, tartaric acid, malonic acid, succinic acid and salts thereof. Specific examples of suitable materials and their amounts are described in United States Patent Application Publication No. 2004/0163736 A1 at [0032] to [0041], the cited portion of which being incorporated herein by reference.

[0064] In certain embodiments, the pretreatment composition also comprises a filler, such as a siliceous filler. Non-limiting examples of suitable fillers include silica, mica, montmorillonite, kaolinite, asbestos, talc, diatomaceous earth, vermiculite, natural and synthetic zeolites, cement, calcium silicate, aluminum silicate, sodium aluminum silicate, aluminum polysilicate, alumina silica gels, and glass particles. In addition to the siliceous fillers other finely divided particulate substantially water-insoluble fillers may also be employed. Examples of such optional fillers include carbon black, charcoal, graphite, titania, iron, copper oxide, zinc oxide, antimony oxide, zirconia, magnesia, alumina, molybdenum disulfide, zinc sulfide, barium sulfate, strontium sulfate, calcium carbonate, and magnesium carbonate.

[0065] As indicated, in certain embodiments, the pretreatment composition is substantially or, in some cases, completely free of chromate and/or heavy metal phosphate. As used herein, the term “substantially free” when used in reference to the absence of chromate and/or heavy metal phosphate, such as zinc phosphate, in the pretreatment composition means that these substances are not present in the composition to such an extent that they cause a burden on the environment. That is, they are not substantially used and the formation of sludge, such as zinc phosphate, formed in the case of using a treating agent based on zinc phosphate, is eliminated.

[0066] Moreover, in certain embodiments, the pretreatment composition is substantially free, or, in some cases, completely free of any organic materials. As used herein, the term “substantially free”, when used with reference to the absence of organic materials in the composition, means that any organic materials are present in the composition, if at all, as an incidental impurity. In other words, the presence of any organic material does not affect the properties of the composition. As used herein, the term “completely free” means that there is no organic material in the composition at all.

[0067] In certain embodiments, the film coverage of the residue of the pretreatment coating composition generally ranges from 1 to 1000 milligrams per square meter (mg/m²), such as 10 to 400 mg/m². The thickness of the pretreatment coating can vary, but it is generally very thin, often having a thickness of less than 1 micrometer, in some cases it is from 1 to 500 nanometers, and, in yet other cases, it is 10 to 300 nanometers.

[0068] Following contact with the pretreatment solution according to any of the above embodiments, the substrate may be rinsed with water and dried.

Additional Coating Composition or Compositions after Pretreatment

[0069] In certain embodiments of the methods of the present invention, after the substrate is contacted with the acid and optional alkaline cleaner and optionally with a pretreatment composition, it is then contacted with a coating composition comprising a film-forming resin. Any suitable technique may be used to contact the substrate with such a coating composition, including, for example, brushing, dipping, flow coating, spraying and the like. In certain embodiments, however, as described in more detail below, such contacting comprises an electrocoating step wherein an electrodepositable composition is deposited onto the metal substrate by electrodeposition.

[0070] As used herein, the term “film-forming resin” refers to resins that can form a self-supporting continuous film on at least a horizontal surface of a substrate upon removal of any diluents or carriers present in the composition or upon curing at ambient or elevated temperature. Conventional film-forming resins that may be used include, without limitation, those typically used in automotive OEM coating compositions, automotive refinish coating compositions, industrial coating compositions, architectural coating compositions, coil coating compositions, and aerospace coating compositions, among others.

[0071] In certain embodiments, the coating composition comprises a thermosetting film-forming resin. As used herein, the term “thermosetting” refers to resins that “set” irreversibly upon curing or crosslinking, wherein the polymer chains of the polymeric components are joined together by covalent bonds. This property is usually associated with a cross-linking reaction of the composition constituents often induced, for example, by heat or radiation. Curing or crosslinking reactions also may be carried out under ambient conditions. Once cured or crosslinked, a thermosetting resin will not melt upon the application of heat and is insoluble in solvents. In other embodiments, the coating composition comprises a thermoplastic film-forming resin. As used herein, the term “thermoplastic” refers to resins that comprise polymeric components that are not joined by covalent bonds and thereby can undergo liquid flow upon heating and are soluble in solvents.

[0072] As previously indicated, in certain embodiments, the substrate is contacted with a coating composition comprising a film-forming resin by an electrocoating step wherein an electrodepositable composition is deposited onto the metal substrate by electrodeposition. In the process of electrodeposition, the metal substrate being treated, serving as an electrode, and an electrically conductive counter electrode are placed in contact with an electrolyte, electrodepositable composition. Upon passage of an electric current between the electrode and counter electrode while they are in contact with the electrodepositable composition, an adherent film of the electrodepositable composition will deposit in a substantially continuous manner on the metal substrate.

[0073] Electrodeposition is usually carried out at a constant voltage in the range of from 1 volt to several thousand volts, typically between 50 and 500 volts. Current density is usually between 1.0 ampere and 15 amperes per square foot (10.8 to 161.5 amperes per square meter) and tends to decrease quickly during the electrodeposition process, indicating formation of a continuous self-insulating film.
The electrodepositable composition utilized in certain embodiments of the present invention often comprises a resinous phase dispersed in an aqueous medium wherein the resinous phase comprises: (a) an active hydrogen group-containing ionic electrodepositable resin, and (b) a curing agent having functional groups reactive with the active hydrogen groups of (a). In certain embodiments, the electrodepositable compositions utilized in certain embodiments of the present invention contain, as a main film-forming polymer, an active hydrogen-containing ionic, often cationic, electrodepositable resin. A wide variety of electrodepositable film-forming resins are known and can be used in the present invention so long as the polymers are “water dispersible,” i.e., adapted to be solubilized, dispersed or emulsified in water. The water dispersible polymer is ionic in nature, that is, the polymer will contain anionic functional groups to impart a negative charge or, as is often preferred, cationic functional groups to impart a positive charge.

Examples of film-forming resins suitable for use in anionic electrodepositable compositions are base-solubilized, carboxylic acid containing polymers, such as the reaction product or adduct of a drying oil or semi-drying fatty acid ester with a dicarboxylic acid or anhydride; and the reaction product of a fatty acid ester, unsaturated acid or anhydride and any additional unsaturated modifying materials which are further reacted with polyol. Also suitable are the at least partially neutralized interpolymer esters of hydroxy-alkyl esters of unsaturated carboxylic acids, unsaturated carboxylic acid and at least one other ethylenically unsaturated monomer. Still another suitable electrodepositable film-forming resin comprises an alkyl-aminoplast vehicle, i.e., a vehicle containing an alkyl resin and an amine-aldehyde resin. Yet another anionic electrodepositable resin composition comprises mixed esters of a resinous polyol, such as is described in U.S. Pat. No. 3,749,657 at col. 9, lines 1 to 75 and col. 10, lines 1 to 13, the cited portion of which being incorporated herein by reference. Other acid functional polymers can also be used, such as phosphated polyepoxide or phosphated acrylic polymers as are known to those skilled in the art.

As aforementioned, it is often desirable that the active hydrogen-containing ionic electrodepositable resin (a) is cationic and capable of deposition on a cathode. Examples of such cationic film-forming resins include amine salt containing resins, such as the acid-solubilized reaction products of polyepoxides and primary or secondary amines, such as those described in U.S. Pat. Nos. 3,663,389; 3,984,299; 3,947,338; and 3,947,339. Often, these amine salt group-containing resins are used in combination with a blocked isocyanate curing agent. The isocyanate can be fully blocked, as described in U.S. Pat. No. 3,984,299, or the isocyanate can be partially blocked and reacted with the resin backbone, such as is described in U.S. Pat. No. 3,947,338. Also, one-component compositions as described in U.S. Pat. No. 4,134,866 and DE-OS No. 2,707,405 can be used as the film-forming resin. Besides the epoxy-amine reaction products, film-forming resins can also be selected from cationic acrylic resins, such as those described in U.S. Pat. Nos. 3,455,806 and 3,928,157.

Besides amine salt group-containing resins, quaternary ammonium salt group-containing resins can also be employed, such as those formed from reacting an organic polyepoxide with a tertiary amine salt as described in U.S. Pat. Nos. 3,962,165; 3,975,346; and 4,001,101. Examples of other cationic resins are tertiary sulfonium salt group-containing resins and quaternary phosphonium salt-group containing resins, such as those described in U.S. Pat. Nos. 3,793,278 and 3,984,922, respectively. Also, film-forming resins which cure via transesterification, such as described in European Application No. 12463 can be used. Further, cationic compositions prepared from Mannich bases, such as described in U.S. Pat. No. 4,134,932, can be used.

In certain embodiments, the resins present in the electrodepositable composition are positively charged resins which contain primary and/or secondary amine groups, such as described in U.S. Pat. Nos. 3,663,389; 3,947,338; and 4,116,900. In U.S. Pat. No. 3,947,339, a polyketimine derivative of a polyamine, such as diethylene triamine or triethylenetetramine, is reacted with a polyepoxide. When the reaction product is neutralized with acid and dispersed in water, free primary amine groups are generated. Also, equivalent products are formed when polyepoxide is reacted with excess polyamines, such as diethylene triamine and triethylenetetramine, and the excess polyamine vacuum stripped from the reaction mixture, as described in U.S. Pat. Nos. 3,663,389 and 4,116,900.

In certain embodiments, the active hydrogen-containing ionic electrodepositable resin is present in the electrodepositable composition in an amount of 1 to 60 percent by weight, such as 5 to 25 percent by weight, based on total weight of the electrodeposit composition bath.

As indicated, the resinous phase of the electrodepositable composition often further comprises a curing agent adapted to react with the active hydrogen groups of the ionic electrodepositable resin. For example, both blocked organic polyisocyanate and aminoplast curing agents are suitable for use in the present invention, although blocked isocyanates are often preferred for cathodic electrodeposition.

Aminoplast resins, which are often the preferred curing agent for anionic electrodeposition, are the condensation products of amines or amides with aldehydes. Examples of suitable amine or amides are melamine, benzoguanamine, urea and similar compounds. Generally, the aldehyde employed is formaldehyde, although products can be made from other aldehydes, such as acetaldehyde and furfural. The condensation products contain methyol groups or similar alkylol groups depending on the particular aldehyde employed. Often, these methyol groups are etherified by reaction with an alcohol, such as a monohydric alcohol containing from 1 to 4 carbon atoms, such as methanol, ethanol, isopropanol, and n-butanol. Aminoplast resins are commercially available from American Cyanamid Co. under the trademark CYMEL and from Monsanto Chemical Co. under the trademark RESIMENE.

The aminoplast curing agents are often utilized in conjunction with the active hydrogen containing anionic electrodepositable resin in amounts ranging from 5 percent to 60 percent by weight, such as from 20 percent to 40 percent by weight, the percentages based on the total weight of the resin solids in the electrodepositable composition.

As indicated, blocked organic polyisocyanates are often used as the curing agent in cathodic electrodeposition compositions. The polyisocyanates can be fully blocked as described in U.S. Pat. No. 3,984,299 at col. 1, lines 1 to 68, col. 2, and col. 3, lines 1 to 15, or partially blocked and reacted with the polymer backbone as described in U.S. Pat. No. 3,947,338 at col. 2, lines 65 to 68, col. 3, and col. 4 lines 1 to 30, the cited portions of which being incorporated herein by reference. By “blocked” is meant that the isocyanate groups have been reacted with a compound so that the resultant blocked isocyanate group is stable to active hydrogens at...
ambient temperature but reactive with active hydrogens in the film forming polymer at elevated temperatures usually between 90° C. and 200° C.

[0085] Suitable polyisocyanates include aromatic and aliphatic polyisocyanates, including cycloaliphatic polyisocyanates and representative examples include diphenylmethane-4,4'-isocyanate (MDI), 2,4- or 2,6-toluene diisocyanate (TDI), including mixtures thereof, p-phenylene diisocyanate, tetramethylene and hexamethylene disiocyanates, dicyclohexylmethane-4,4'-diisocyanate, isophorone diisocyanate, mixtures of phenylmethane-4,4'-diisocyanate and polyisocyanate polyphenylisocyanate. Higher polyisocyanates, such as triisocyanates can be used. An example would include triphenylmethane-4,4',4'-trisosocyanate. Isocyanate (-)-prepolymers with polyols such as neopentyl glycol and trimethylolpropane and with polymeric polyols such as poly-caprolactone diols and triols (NCO/OH equivalent ratio greater than 1) can also be used.

[0086] The polyisocyanate curing agents are typically utilized in conjunction with the active hydrogen containing ionic electrodepositable resin in amounts ranging from 5 percent to 60 percent by weight, such as from 20 percent to 50 percent by weight, the percentages based on the total weight of the resin solids of the electrodepositable composition.

[0087] In certain embodiments, the coating composition comprising a film-forming resin also comprises yttrium. In certain embodiments, yttrium is present in such compositions in an amount from 10 to 10,000 ppm, such as not more than 5,000 ppm, and, in some cases, not more than 1,000 ppm, of total yttrium (measured as elemental yttrium).

[0088] Both soluble and insoluble yttrium compounds may serve as the source of yttrium. Examples of yttrium sources suitable for use in lead-free electrodepositable coating compositions are soluble organic and inorganic yttrium salts such as yttrium acetate, yttrium chloride, yttrium formate, yttrium carbonate, yttrium sulfamate, yttrium lactate and yttrium nitrate. When the yttrium is to be added to an electrocoat bath as an aqueous solution, yttrium nitrate, a readily available yttrium compound, is a preferred yttrium source. Other yttrium compounds suitable for use in electrodepositable compositions are organic and inorganic yttrium compounds such as yttrium oxide, yttrium bromide, yttrium hydroxide, yttrium molybdate, yttrium sulfate, yttrium silicate, and yttrium oxalate. Organoyttrium complexes and yttrium metal can also be used. When the yttrium is to be incorporated into an electrocoat bath as a component in the pigment paste, yttrium oxide is often the preferred source of yttrium.

[0089] The electrodepositable compositions described herein are in the form of an aqueous dispersion. The term “dispersion” is believed to be a two-phase transparent, translucent or opaque resinous system in which the resin is in the dispersed phase and the water is in the continuous phase. The average particle size of the resinous phase is generally less than 1.0 and usually less than 0.5 microns, often less than 0.15 micron.

[0090] The concentration of the resinous phase in the aqueous medium is often at least 1 percent by weight, such as from 2 to 60 percent by weight, based on total weight of the aqueous dispersion. When such compositions are in the form of a resin concentrates, they generally have a resin solids content of 20 to 60 percent by weight based on weight of the aqueous dispersion (TDI), including mixtures thereof.

[0091] The electrodepositable compositions described herein are often supplied as two components: (1) a clear resin feed, which includes generally the active hydrogen-containing ionic electrodepositable resin, i.e., the main film-forming polymer, the curing agent, and any additional water-dispersible, non-pigmented components; and (2) a pigment paste, which generally includes one or more colorants (described below), a water-dispersible grind resin which can be the same or different from the main-film forming polymer, and, optionally, additives such as wetting or dispersing aids. Electrodeposition bath components (1) and (2) are dispersed in an aqueous medium which comprises water and, usually, coalescing solvents.

[0092] As aforementioned, besides water, the aqueous medium may contain a coalescing solvent. Useful coalescing solvents are often hydrocarbons, alcohols, esters, ethers and ketones. The preferred coalescing solvents are often alcohols, polyols and ketones. Specific coalescing solvents include isopropanol, butanol, 2-ethylhexanol, isophorone, 2-methoxy pentanone, ethylene and propylene glycol and the mono-ethyl monobutyl and monoethyl ethers of ethylene glycol. The amount of coalescing solvent is generally between 0.01 and 25 percent, such as from 0.05 to 5 percent by weight based on total weight of the aqueous medium.

[0093] In addition, a colorant and, if desired, various additives such as surfactants, wetting agents or catalyst can be included in the coating composition comprising a film-forming resin. 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 composition in any suitable form, such as discrete particles, dispersions, solutions and/or flakes. A single colorant or a mixture of two or more colorants can be used.

[0094] 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 dispersible under the conditions of use. A colorant can be organic or inorganic and can be agglomerated or non-agglomerated. Colorants can be incorporated 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.

[0095] Example pigments and/or pigment compositions include, but are not limited to, carboxzole dioxazine crude pigment, azo, monoozo, disazo, naphthol AS, salt type (lakes), benzimidazolone, condensation, metal complex, isoindolinone, isoindoline and polycyclic phthalocyanine, quinacridone, perylene, perinone, diketopyrrolo pyrrole, thiodindigo, anthraquinone, indanthrene, anthrapyrimidine, flavanthrone, pyranthrone, anthanthrene, dioxygenase, triarylfuran, 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.

[0096] Example dyes include, but are not limited to, those that are solvent and/or aqueous based such as phthalo green or blue, iron oxide, bisanthrene vanadate, anthraquinone, perylene, aluminum and quinacridone.

[0097] 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 MAXTONE 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 nanocrystallite 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 μm. Example nanoparticle dispersions and methods for making them are identified in U.S. Pat. No. 6,875,800 B2, which is incorporated herein by reference. Nanoparticle dispersions can also be produced by crystallization, precipitation, gas phase condensation, and chemical attrition (i.e., partial dissolution). In order to minimize reagglomeration 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 2005-0267348 A1, 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, which is also incorporated herein by reference.

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, goniometer and/or color-change. Additional special effect compositions can provide other perceptible properties, such as opacity or texture. In certain embodiments, 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, incorporated herein by reference. Additional color effect compositions can include transparent coated mica and/or synthetically 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 embodiments, a photosensitive composition and/or photochromic composition, which reversibly alters its color when exposed to one or more light sources, can be used. 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 certain embodiments, 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 certain embodiments, 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 certain embodiments 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, incorporated herein by reference.

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

After deposition, the coating is often heated to cure the deposited composition. The heating or curing operation is often carried out at a temperature in the range of from 120 to 250°C, such as from 120 to 190°C, for a period of time ranging from 10 to 60 minutes. In certain embodiments, the thickness of the resultant film is from 10 to 50 microns.

Electrodepositable Coating Composition without Pretreatment

In certain embodiments of the methods of the present invention, after the substrate is contacted with the acid and without the subsequent contact with a pretreatment composition, it may then be contacted with an electrodepositable coating composition comprising (i) a film-forming compound and (ii) a source of yttrium.

As defined herein, the term “without the subsequent contact with a pretreatment composition” means that the substrate has not been contacted with a composition that, upon contact with the substrate, react(s) with and chemically alters the substrate surface and binds to it to form a protective layer. This specifically includes any of the pretreatment compositions comprising a group IIIB and/or group IVB metal as described above, and further includes other known pretreatment compositions such as, for example, zinc or iron phosphate-type conversion or pretreatment coatings.

In certain embodiments, the electrodepositable coating composition may be formed in accordance with U.S. patent application Ser. No. 12/693,626, which is herein incorporated by reference, and may also include (iii) a silane that does not contain an ethynelically unsaturated double bond. In certain embodiments, the coating composition may be formed in accordance with U.S. patent application Ser. No. 12/693,626 and may further also include (iii) an aminosilane, which could or could not contain an ethynelically unsaturated double bond.

In some embodiments, when the film-forming polymer comprises a reactive functional group, the coating composition further comprises (iv) a curing agent that is reactive with a reactive functional group of the film-forming polymer.

A wide variety of film-forming polymers, which are known in the art, can be used as component (i) so long as the polymers are “water dispersible.” As used herein, “water dispersible” means that a material is adapted to be solubilized,
dispersed, and/or emulsified in water. The film-forming polymers used in the present invention are ionic in nature. Accordingly, in some embodiments, the film-forming polymer is cationic. In other words, the film-forming polymer comprises cationic salt groups, generally prepared by neutralizing a functional group on the film-forming polymer with an acid, which enables the film-forming polymer to be electrodeposited onto a cathode.

Examples of film-forming polymers suitable for use in cationic electrocoating coating compositions include, without limitation, cationic polymers derived from a polyethylene oxide, an acrylic, a polyurethane, and/or polyester. In certain embodiments, the film-forming polymer comprises reactive functional groups. As used herein, the phrase "reactive functional group" means hydroxyl, carboxyl, carbamate, epoxy, isocyanate, acetoacetate, amine-salt, mercaptan, or combinations thereof. It should be noted that in some embodiments, the film-forming polymer is a copolymer of the polymers listed in the preceding sentence. In some embodiments, the cationic polymer can be derived by reacting a polyethylene oxide containing polymer with a cationic salt group former. As used herein, "cationic salt group former" means a material that is reactive with epoxy groups and which can be acidified before, during, or after reaction with the epoxy groups to form cationic salt groups. Suitable materials that can be used as the cationic salt group former include amines such as primary or secondary amines, which can be acidified after reaction with the epoxy groups to form amine salt groups, or tertiary amines, which can be acidified prior to reaction with the epoxy groups and which after reaction with the epoxy groups form quaternary ammonium salt groups. Examples of other cationic salt group formers are sulfides which can be mixed with acid prior to reaction with the epoxy groups and form ternary sulfonium salt groups upon subsequent reaction with the epoxy groups.

In certain embodiments, the film-forming polymer that is used in the present invention comprises the reaction product of an epoxy functional compound (e.g., EPON 880) and a phenolic hydroxyl group-containing material such as bisphenol A, which is a polyhydric phenol. In some embodiments, the film-forming polymer (i) described in the preceding sentence can be reacted with an amine, such as aminopropyltriethoxysilane (APDEA) and dimethylaminopropylamine (DMPA), in order to make the film-forming polymer water dispersible. In certain embodiments, ketone may be reacted with the backbone of the film-forming polymer thereby forming ketone arms that extend pendant to the backbone. When the polymer is dispersed in a water/acid mixture, the ketone arms will hydrolyze and form primary amines. Accordingly, in some embodiments, the electrodepositable coating compositions that are disclosed in U.S. Pat. Nos. 5,633,297, 5,820,987, and/or 5,936,012 can be used with the present invention.

Various corrosion inhibitors may be used as component (a) in the present invention. Suitable corrosion inhibitors include, without limitation, rare earth metals, bismuth, copper, zinc, silver, zirconium, or combinations thereof. In certain embodiments, an yttrium compound or a cerium compound, or a mixture of an yttrium and cerium compound, may be used as the corrosion inhibitor. Yttrium and cerium compounds, as defined herein, include their respective salts and hereinafter may be referred to simply as yttrium compounds or cerium compounds. They may also be included in the list of potential compounds comprising a source or yttrium or a source of cerium.

Various yttrium compounds may be used as component (ii) in the present invention. For example, the yttrium compounds may include, without limitation, yttrium formate, yttrium acetate, yttrium lactate, yttrium sulfate, yttrium methanol sulfate, yttrium nitrate, or combinations thereof. In some embodiments, yttrium comprises ≤5 weight % of the total resin solids of the electrodepositable coating composition. In other embodiments, yttrium comprises ≥0.15 weight % of the total resin solids of the electrodepositable coating composition. In certain embodiments, the amount of yttrium can range between any combination of values, which were recited in the preceding sentences, inclusive of the recited values. For example, in certain embodiments, the amount of yttrium can range from 0.20 weight % to 2 weight % of the total resin solids of the electrodepositable coating composition.

Various cerium compounds may be used as component (ii) in the present invention. For example, the cerium compounds may include ammonium cerium nitrate, ammonium cerium sulfate, cerium acetate, cerium bromide, cerium carbonate, cerium chloride, cerium fluoride, cerium iodide, cerium nitrate, cerium molybdate, cerium oxide, cerium oxalate, cerium phosphate, and cerium sulfate. In some embodiments, cerium comprises ≤5 weight % of the total resin solids of the electrodepositable coating composition. In other embodiments, cerium comprises ≥0.15 weight % of the total resin solids of the electrodepositable coating composition. In certain embodiments, the amount of cerium can range between any combination of values, which were recited in the preceding sentences, inclusive of the recited values. For example, in certain embodiments, the amount of cerium can range from 0.20 weight % to 2 weight % of the total resin solids of the electrodepositable coating composition.

Various combinations of yttrium compounds and cerium compounds, as described in the previous paragraphs, may be used as component (ii) in the present invention. In some embodiments, the combination of yttrium and cerium comprises ≤5 weight % of the total resin solids of the electrodepositable coating composition. In other embodiments, the combination of yttrium and cerium comprises ≥0.15 weight % of the total resin solids of the electrodepositable coating composition. In certain embodiments, the amount of yttrium and cerium can range between any combination of values, which were recited in the preceding sentences, inclusive of the recited values. For example, in certain embodiments, the amount of yttrium and cerium can range from 0.20 weight % to 2 weight % of the total resin solids of the electrodepositable coating composition.

If (i) the film-forming polymer comprises reactive functional groups, such as those described above, then the electrodepositable coating composition may further comprise (iv) a crosslinking agent ("curing agent") that is reactive with the reactive functional groups of the polymer. Suitable crosslinking agents include, without limitation, aminoplasts, polyisocyanates (including blocked isocyanates), polyepoxides, beta-hydroxyalkylamides, polycrudes, anhydrides, organometallic acid-functional materials, polyanines, polyanimes, cyclic carbonates, siloxanes, or combinations thereof. In some embodiments, the curing agent may comprise from 30 weight % to 40 weight % of the total resin solids of the coating composition.
[0116] In certain embodiments, the electrodepositable coating composition may further comprise (v) a curing catalyst, which may be used to catalyze the reaction between the crosslinking agent and the reactive functional groups of the film-forming polymer. Suitable curing catalysts that may be used as component (v) include, without limitation, organotin compounds (e.g., dibutyltin oxide, dioctyltin oxide) and salts thereof (e.g., dibutyltin diacetate); other metal oxides (e.g., oxides of cerium, zirconium and/or bismuth) and salts thereof (e.g., bismuth sulfate and/or bismuth lactate), bicyclic guanidine (as disclosed in U.S. patent application Ser. No. 11/835,600), or combinations thereof.

[0117] The electrodepositable coating composition disclosed herein is typically supplied as two components: (1) a main vehicle (“clear resin feed”) and (2) a grind vehicle (“pigment paste”). In general, (1) the main vehicle comprises (a) a film-forming polymer (“an active hydrogen-containing ionic salt-containing resin”), (b) a crosslinking agent, and (c) any additional water-dispersible, non-pigmented components (e.g., catalysts, hindered amine light stabilizers). In general, (2) the grind vehicle comprises (d) one or more pigments (e.g., titanium dioxide, carbon black), (e) a water-dispersible grind resin, which can be the same or different from the film-forming polymer, and, optionally, (f) additives such as catalysts, antioxidants, biocides, defoamers, surfactants, wetting agents, dispersing aids, clays, hindered amine light stabilizers, UV light absorbers and stabilizers, or combinations thereof. An electrodeposition bath, which contains the electrodepositable coating composition of the present invention, can be prepared by dispersing components (1) and (2) in an aqueous medium which comprises water and, usually, coalescing solvents. The (ii) yttrium and/or the (iii) silane, which are used in the electrodepositable coating composition of the present invention, may be incorporated into the main vehicle, the grind vehicle, or post-added to a bath that is prepared with components (1) and (2). Alternatively, components (1) and (2) may also be provided as a single component.

[0118] The electrodepositable coating composition described herein may be applied alone or as part of a coating system that can be deposited onto a number of different substrates. The coating system typically comprises a number of coating layers. A coating layer is typically formed when a coating composition that is deposited onto the substrate is substantially cured by methods known in the art (e.g., by thermal heating).

[0119] After the electrodepositable coating composition is cured, a primer-surfacer coating composition is applied onto at least a portion of the electrodepositable coating composition. The primer-surfacer coating composition is typically applied to the electrodepositable coating layer and cured prior to a subsequent coating composition being applied over the primer-surfacer coating composition.

[0120] The primer-surfacer layer that results from the primer-surfacer coating composition serves to enhance chip resistance of the coating system as well as aid in the appearance of subsequently applied layers (e.g., color imparting coating composition and/or substantially clear coating composition). 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. Suitable primers and primer-surfacer coating compositions include spray applied primers, as are known to those skilled in the art. Examples of suitable primers include several available from PPG Industries, Inc., Pittsburgh, Pa., as DPX-1791, DPX-1804, DSPX-1537, GPXH-5379, OPP-2645, PCV-70118, and 1177-225A. Another suitable primer-surfacer coating composition that can be utilized in the present invention is the primer-surfacer described in U.S. patent application Ser. No. 11/773,482, which is incorporated in its entirety herein by reference.

[0121] It should be noted that in some embodiments, the primer-surfacer coating composition is not used in the coating system. Therefore, a color imparting basecoat composition can be applied directly onto the cured electrodepositable coating composition.

[0122] 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 composition known in the art may be used in the present invention. It should be noted that these basecoat compositions typically comprise a colorant.

[0123] 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, which are incorporated in their entirety herein by reference, 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).

[0124] 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. A 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.

[0125] 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.

[0126] Example pigments and/or pigment compositions include, but are not limited to, carboxylate dioxazine crude pigments used herein “primer, disazo, napthol AS, salt type (lakes), benzimidazolone, condensation, metal complex, isoidolfinone, isoindoline and polycyclic phthalocyanine, quinacridone, perylene, perinone, diketopyrrolo pyrrole, thiodindigo, anthraquinone, indanthrone, anthrapyrimidine, flavanthrone, pyranthrene, anthanthrone, dioxygen, triaryl-carbonium, quinophthalone pigments, diketo pyrrolo pyrrole red ("DPPO 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 phthalo 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 806 commercially available from Degussa Inc., CHARISMA COLORANTS® and MAX- TONER 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, which is incorporated herein by reference. Nanoparticle dispersions can also be produced by crystallization, precipitation, gas phase condensation, and chemical attrition (i.e., partial dissolution). In order to minimize re-aggregation 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 discrete “composite microparticles”, which comprise a nanoparticle and a resin coating on the nanoparticle, is dispersed. Example dispersions of resin-coated nanoparticles and methods for making them are identified in U.S. Patent Publication No. 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, which are also incorporated herein by reference.

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, goniocromism 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, incorporated herein by reference. 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. patent 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.

In addition to the materials described above, the coating composition can also comprise an organic solvent. Suitable organic solvents that can be used in the coating composition include any of those listed in the preceding paragraphs as well as butyl acetate, xylene, methyl ethyl ketone, or combinations thereof.

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, both coating compositions may be cured simultaneously.

[0138] The coating compositions may be cured using any technique known in the art such as, without limitation, thermal energy, ultraviolet light, ultraviolet, actinic radiation, or by any combination thereof. In certain embodiments, the curing operation can be carried out at temperatures \( \geq 10^\circ C \). In other embodiments, the curing operation can be carried out at temperature \( \leq 246^\circ C \). In certain embodiments, the curing operation can be 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.

[0139] In certain embodiments, one or more of the coating compositions described herein is 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.

[0140] 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 \( \leq 125 \) microns, such as \( \leq 60 \) microns. For example, the dry film thickness can range from 15 microns to 60 microns.

[0141] 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.

[0142] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications which are within the spirit and scope of the invention, as defined by the appended claims.

EXAMPLES

[0143] Coating compositions, panels, and testing methods used in these Examples were prepared and described as follows:

[0144] Alkaline Cleaner 1: Chemkleen 2010L/P/181ALP, a commercial alkaline cleaner available from PPG Industries, Inc.

[0145] Alkaline Cleaner 1A: Experimental alkaline cleaner with a composition similar to Chemkleen 166HP, commercially available from PPG Industries, Inc.

[0146] Acid Cleaner 2—A citric acid cleaner prepared as follows. First, 468.4 g of anhydrous citric acid was dissolved in 18,000 g of water. Next, 103.4 g of a commercial surfactant package, Chemkleen 171-12, was added to the mixture. Finally, potassium hydroxide was added to the mixture to adjust the pH of the resultant mixture to 4.5.

[0147] Pretreatment Composition 1: CHEMFOS 700, immersion applied tricyclonic Zn phosphate (a commercial pretreatment product available from PPG Industries, Inc.).

[0148] Electrodepositable Paint Composition 1: Environprime® 7000P, a cationic electrocoat commercially available from PPG Industries, Inc.

[0149] Electrodepositable Paint Composition 2: Yttrium-containing Electrodepositable Paint prepared in accordance with Paint 4 in Table 1 (paragraph [0074]) of U.S. patent application Ser. No. 12/693,626.)

[0150] Phosphated panels were purchased from ACT.

[0151] Test 1: 40 cycles of GM9540P (Cycle B)

[0152] Test 2: 24 hours in a cathodic disbondment test. The test involves a scribed panel submerged into a sodium sulfate solution where a current of 10 mA is passed through the panel. After 24 hours, tape is used to remove delaminated paint and the width of the delaminated area is measured.

Comparative Results

Experiment 1

Comparison of Corrosion Resistance on Cleaned Panels Subsequently Coated with Electrodepositable Coating Composition 1—Alkaline Cleaner 1 Vs. Acid Cleaner 2

[0153] Cold-rolled steel panels (ACT Panels) were cleaned using Cleaner 1 or Cleaner 2, rinsed with deionized water, and dried using forced hot air. The panels were electrocoated in Electrodepositable Paint Composition 1 and cured for 25 minutes @ 177° C in an electric oven. The dry film thickness was 0.0005-0.0010 inches. Samples were then scribed vertically and placed in Test 1. Average scribe creep results are shown in Table 1 below.

<table>
<thead>
<tr>
<th>Cleaner</th>
<th>Avg Scribe Creep (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 - 2' Spray</td>
<td>18.7</td>
</tr>
<tr>
<td>#2 - 4' Spray</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Experiment 2

Comparison of Corrosion Resistance on Cleaned Panels Subsequently Coated with Electrodepositable Coating Composition 2—Alkaline Cleaner 1A Vs. Acid Cleaner 2

[0154] Cold-rolled steel panels (ACT Panels) were cleaned using Alkaline Cleaner 1A or Acid Cleaner 2, rinsed with deionized water, and dried using forced hot air. The panels were electrocoated in Electrodepositable Paint Composition 2 and cured for 25 minutes @ 177° C in an electric oven. The dry film thickness was 0.0005-0.0010 inches. Samples were then scribed vertically and placed in Test 1. Average scribe creep results are shown in Table 2 below.

<table>
<thead>
<tr>
<th>Cleaner</th>
<th>Avg Scribe Creep (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 - 2' Spray</td>
<td>18.7</td>
</tr>
<tr>
<td>#2 - 4' Spray</td>
<td>7.6</td>
</tr>
</tbody>
</table>
TABLE 2

<table>
<thead>
<tr>
<th>Cleaner</th>
<th>Avg Scribe Creep (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1A - 2' Immersion</td>
<td>9.5</td>
</tr>
<tr>
<td>#2 - 4' Spray</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Experiment 3

Comparison of Yttrium Deposition on Cleaned Panels—Alkaline Cleaner 1A Alone Vs. Alkaline Cleaner 1A Followed by Acid Cleaner 2

Cold-rolled steel panels (ACT Panels) were cleaned using Alkaline Cleaner 1A alone, or Alkaline Cleaner 1A followed by Acid Cleaner 2, and rinsed with deionized water. The panels were then placed in a solution of yttrium sulfate (800 ppm yttrium) buffered to a pH of 5.5. 80 mA of current was passed through the solution for 2 minutes at room temperature. Panels were then rinsed with deionized water and dried using forced air. After drying, the amount of yttrium deposited on the panels was measured by wave-dispersive X-ray fluorescence. The results are shown in Table 3 below:

TABLE 3

<table>
<thead>
<tr>
<th>Cleaner</th>
<th>wt % Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1A 2' Spray</td>
<td>0.82</td>
</tr>
<tr>
<td>#2 2' Spray</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Experiment 4

Comparison of Corrosion Resistance on Cleaned Panels Subsequently Coated with Electrodepositable Coating Composition 2—Cleaner 1A Vs. Cleaner 1A Followed by Cleaner 2 vs. Cleaner 2 Followed by Cleaner 1A—Ecoated Panels with Corrosion Inhibitor

Cold-rolled steel panels (ACT Panels) were cleaned using Alkaline Cleaner 1A, Alkaline Cleaner 1A followed by Acid Cleaner 2, or Acid Cleaner 2 followed by Alkaline Cleaner 1A, and then rinsed with deionized water. Panels were then dried using forced air. After drying, the panels were electrocoated in Electrodepositable Paint Composition 2 and cured for 25 minutes at 177°F in an electric oven. The dry film thickness was 0.0005-0.0010 inches.

Panels with Pretreatment 1 were purchased from ACT and electrocoated with Electrodepositable Paint Composition 1 for comparison.

Samples were then scribed vertically and placed in Test 2. The results are shown Table 4 below:

TABLE 4

<table>
<thead>
<tr>
<th>Step 1</th>
<th>Step 2</th>
<th>Scribe Creep (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaner #1A - 2' Spray</td>
<td>Cleaner #1A - 30 sec Spray</td>
<td>5.52</td>
</tr>
<tr>
<td>Cleaner #2 - 3' Spray</td>
<td>Cleaner #1A - 3' Spray</td>
<td>3.03</td>
</tr>
<tr>
<td>Cleaner #2 - 3' Spray</td>
<td>Cleaner #1A - 30 sec Spray</td>
<td>3.00</td>
</tr>
<tr>
<td>Phosphate (Pretreatment #1)</td>
<td></td>
<td>5.34</td>
</tr>
</tbody>
</table>

We claim:

1. A method comprising:
   (a) contacting a substrate with an acid; and then
   (b) contacting the substrate with an electrodepositable coating composition comprising (i) a film-forming polymer; and (ii) a corrosion inhibitor;
   with the proviso that the method does not comprise contacting the substrate with a pretreatment composition prior to step (b).

2. The method of claim 1, wherein said corrosion inhibitor comprises a rare earth metal, a lanthanide, or combinations thereof,

3. The method of claim 1, wherein said corrosion inhibitor comprises a source of yttrium.

4. The method of claim 3, wherein said source of yttrium comprises an yttrium compound.

5. The method of claim 1, wherein said corrosion inhibitor comprises a source of cerium.

6. The method of claim 5, wherein said source of cerium comprises a cerium compound.

7. The method of claim 1, wherein said corrosion inhibitor comprises a source of yttrium and a source of cerium.

8. The method of claim 1, wherein said electrodepositable coating composition further comprises (iii) a silane that does not contain an ethylenically unsaturated double bond.

9. The method of claim 1, wherein said acid comprises an organic acid.

10. The method of claim 1, wherein said acid comprises a mineral acid.

11. The method of claim 1, wherein said acid comprises an organic acid, a mineral acid or mixtures thereof.

12. The method of claim 9, wherein said organic acid comprises a carboxylic acid.

13. The method of claim 9, wherein said organic acid comprises citric acid.

14. The method of claim 1 further comprising (c) contacting the substrate with an alkaline cleaner prior to steps (a) and (b).

15. The method of claim 1 further comprising (c) contacting the substrate with an alkaline cleaner prior to step (b) and after step (a).

16. A coated substrate formed in accordance with the method of claim 1.

17. A coated substrate formed in accordance with the method of claim 8.

18. A method for coating a substrate comprising:
   (a) contacting the substrate with an acid; and then
   (b) contacting the substrate with an alkaline cleaner; and then
   (c) contacting the substrate with an electrodepositable coating composition comprising (i) a film-forming polymer; and (ii) a corrosion inhibitor;
   with the proviso that the method does not comprise contacting the substrate with a pretreatment composition prior to step (b).

19. The method of claim 1, wherein said corrosion inhibitor comprises a rare earth metal, a lanthanide, or combinations thereof.

20. A coated substrate formed in accordance with the method of claim 19.

* * * * *