

ELECTRODEPOSITABLE COATING COMPOSITION COMPRISING SILANE AND YTTRIUM

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of U.S. Provisional Application No. 61/147,583 filed January 27, 2009.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] The present invention relates generally to an electrodeposable coating composition.

Background Information

[0003] Electrodeposition as a coating application method involves depositing an electrodeposable coating composition onto a conductive substrate, which is under the influence of an applied electrical potential. Electrodeposition has become increasingly important in the coatings industry because, by comparison with non-electrophoretic coating means, electrodeposition offers increased paint utilization, improved corrosion protection, and low environmental contamination.

[0004] During electrodeposition, the electrodeposable coating composition is deposited onto a substrate that has been pretreated with a pretreatment solution, such as a zinc phosphate pretreatment solution, prior to the electrodeposition process. Elimination of the pretreatment step prior to the electrodeposition process would reduce the costs associated with coating a substrate as well as eliminate any chemical byproducts that are produced during the pretreatment step. Moreover, in an automotive OEM factory setting, elimination of the pretreatment equipment would mean that the size of the factory could potentially be scaled down or that valuable factory space could be reclaimed.

[0005] Accordingly, the present invention is directed to an electrodeposable coating composition that can be applied onto a non-pretreated substrate.

SUMMARY OF THE INVENTION

[0006] The present invention is directed to an electrodeposable coating composition comprising (i) a film-forming polymer, (ii) yttrium, and (iii) a silane that does not contain an ethylenically unsaturated double bond. The present invention is further directed to a substrate coated with such a coating composition.

[0007] The present invention is also directed to an electrodeposable coating composition consisting essentially of (i) a film-forming polymer comprising reactive functional groups, (ii)

yttrium, (iii) a silane that does not contain an ethylenically unsaturated double bond; (iv) a crosslinking agent that is reactive with the reactive functional groups of the film-forming polymer; and (v) a catalyst.

[0008] The present invention is also directed to an electrodepositable coating composition comprising (i) a film-forming polymer, (ii) yttrium, and (iii) an aminosilane. The present invention is further directed to a substrate coated with such a coating composition.

DETAILED DESCRIPTION OF THE INVENTION

[0009] As used herein, unless otherwise expressly specified, all numbers such as those expressing values, ranges, amounts or percentages may be read as if prefaced by the word "about", even if the term does not expressly appear. Plural encompasses singular and vice versa. For example, although reference is made herein to "a" film forming polymer, "a" yttrium, "a" silane, a combination (a plurality) of these components can be used in the present invention. As used herein, "plurality" means two or more.

[0010] As used herein, "includes" and like terms means "including without limitation."

[0011] When referring to any numerical range of values, such ranges are understood to include each and every number and/or fraction between the stated range minimum and maximum.

[0012] As used herein, "molecular weight" means weight average molecular weight (M_w) as determined by Gel Permeation Chromatography.

[0013] As used herein, the term "cure" refers to a coating wherein any crosslinkable components of the composition are at least partially crosslinked. In certain embodiments, the crosslink density of the crosslinkable components (i.e., the degree of crosslinking) ranges from 5% to 100%, such as 35% to 85%, or, in some cases, 50% to 85% of complete crosslinking. One skilled in the art will understand that the presence and degree of crosslinking, i.e., the crosslink density, can be determined by a variety of methods, such as dynamic mechanical thermal analysis (DMTA) using a Polymer Laboratories MK III DMTA analyzer conducted under nitrogen.

[0014] Reference to any monomer(s) herein refers generally to a monomer that can be polymerized with another polymerizable compound such as another monomer or polymer. Unless otherwise indicated, it should be appreciated that once the monomer components react with one another to form the compound, the compound will comprise the residues of the monomer components.

Electrodepositable Coating Composition

[0015] The present invention is directed to a coating composition comprising (i) a film forming polymer, (ii) yttrium, and (iii) a silane that does not contain an ethylenically unsaturated double bond. In certain embodiments, the coating composition comprises an aminosilane, which could or could not contain an ethylenically 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.

[0016] 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.

[0017] Examples of film-forming polymers suitable for use in cationic electrocoating coating compositions include, without limitation, cationic polymers derived from a polyepoxide, 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, aceto acetate, 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 polyepoxide 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.

[0018] 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 described in the preceding sentence can be reacted with an amine, such as aminopropyl diethanolamine (APDEA) and dimethylaminopropylamine (DMAPA), in order to make the film-forming polymer water dispersible. In certain embodiments, ketimine can be reacted with the backbone of the film-forming polymer thereby forming ketimine arms that extend pendant to the backbone. When the polymer is dispersed in a water/acid mixture, the ketimine 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.

[0019] Various corrosion inhibitors may be used as component (ii) in the present invention. Suitable corrosion inhibitors include, without limitation, rare earth metals, bismuth, copper, zinc, silver, zirconium, or combinations thereof. In certain embodiments, a yttrium compound may be used as the corrosion inhibitor. 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 sulfamate, yttrium methane sulfonate, 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.

[0020] In the present invention, a silane that does not contain an ethylenically unsaturated double bond is typically used as component (iii). However, in certain embodiments, an aminosilane, which may or may not contain an ethylenically unsaturated double bond, may be used in the present invention. As used herein, "ethylenically unsaturated double bond" means a carbon-to-carbon double bond. In certain embodiments, the silane can comprise a functional group such as, without limitation, hydroxyl, carbamate, epoxy, isocyanate, amine, amine-salt, mercaptan, or combinations thereof. Suitable silanes that may be used in the present invention include, without limitation, an aminosilane, a mercaptosilane, or combinations thereof. In some embodiments, the silane can be a mixture of an aminosilane and another material, such as vinyltriacetoxysilane. Accordingly, in certain embodiments, the electrodepositable coating composition can comprise a silane that contains an

ethylenically unsaturated double bond in addition to the silane that does not contain an ethylenically unsaturated double bond.

[0021] 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, polyacids, anhydrides, organometallic acid-functional materials, polyamines, polyamides, cyclic carbonates, siloxanes, or combinations thereof. In some embodiments, the curing agent can comprise from 30 weight % to 40 weight % of the total resin solids of the coating composition.

[0022] 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 sulfamate and/or bismuth lactate), bicyclic guanidine (as disclosed in U.S. Pat. App. No. 11/835,600), or combinations thereof.

[0023] In some embodiments, after the electrodepositable coating composition is applied onto a substrate and cured, the electrodepositable coating composition demonstrates a burst pressure adhesion value of ≥ 500 pounds per square inch (psi), such as from 550 (psi) to 1000 (psi), when subjected to the PATTI ADHESION TESTING METHOD. The PATTI ADHESION TESTING METHOD is a two step process. In the first step, a substrate coated with the cured electrodepositable coating composition, which is to be tested for adhesion properties, is introduced into a QCT-MB cabinet (commercially available from Q-Panel Lab Products) and exposed to condensing humidity at a temperature of 60°C for a time period of 16 hours. The substrate is then removed and any condensation on the surfaces of the coating is removed using a rag. Next, the adhesion properties of the cured electrodepositable coating composition are measured using an Elcometer PATTI 110 adhesion tester (commercially available from Elcometer, Inc.). The method begins by using 3M SCOTCHWELD DP-460 adhesive to glue 1/2 inch diameter aluminum pull stubs (commercially available from Elcometer, Inc.) to the surface of the cured electrodepositable coating composition (the surface onto which the aluminum pull stubs are applied should be lightly sanded and subsequently cleaned with KIMWIPES followed by water then followed by isopropanol wipes). A piston of the Elcometer PATTI 110 adhesion tester is attached to the

aluminum pull stub and a tensile force is applied to the stub using the adhesion tester. The tensile force is increased until an adhesion failure of the cured electrodepositable coating composition is achieved. The amount of force required to cause adhesion failure ("burst pressure adhesion value") can then be calculated using the appropriate conversion charts that are provided with the Elcometer PATTI 110 adhesion tester. As used herein, "burst pressure adhesion value," which is measured in pounds per square inch (psi), is the amount of force required to cause a coating layer to lose adhesion to a substrate.

[0024] In certain embodiments, when the electrodepositable coating composition described herein is compared to an electrodepositable coating composition that does not contain the silane and the corrosion inhibitor (conventional electrodepositable coating composition), the burst pressure of the electrodepositable coating composition will exceed the burst pressure of the conventional electrodepositable coating composition by ≥ 100 pounds per square inch (psi) when subjected to the PATTI ADHESION TESTING METHOD.

[0025] 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 group-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.

Substrate with a Coating System

[0026] 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).

[0027] Suitable substrates that can be coated with the electrodepositable coating composition of the present invention include, without limitation, metal substrates, metal alloy substrates, and/or substrates that have been metallized, such as nickel plated plastic. In some embodiments, the metal or metal alloy can be aluminum and/or steel. For example, the steel substrate could be cold rolled steel, electrogalvanized 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. It will also be understood that, in some embodiments, the substrate may be pretreated with a pretreatment solution, such as a zinc phosphate solution as described in U.S. Pat. Nos. 4,793,867 and 5,588,989. Alternatively, in other embodiments, the substrate is not pretreated with a pretreatment solution prior to coating the substrate with the coating composition described herein.

[0028] In certain embodiments, the electrodepositable coating composition of the present invention is applied over a bare (i.e., non-pretreated) substrate. However, in some embodiments, the electrodepositable coating composition of the present invention can be applied to a substrate that has been pretreated. 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.

[0029] 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. Pat. Application No. 11/773,482, which is incorporated in its entirety herein by reference.

[0030] 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 coating composition can be applied directly onto the cured electrodepositable coating composition.

[0031] In some embodiments, a color imparting coating composition (hereinafter, "basecoat") is deposited onto at least a portion of the primer surfacer coating layer (if present). Any basecoat coating composition known in the art may be used in the present invention. It should be noted that these basecoat coating compositions typically comprise a colorant.

[0032] 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. Patent 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).

[0033] One or more of the coating compositions described herein can comprise colorants and/or other optional materials, which are known in the art of formulated surface coatings. As used herein, the term "colorant" means any substance that imparts color and/or other opacity and/or other visual effect to the composition. The colorant can be added to the coating in any suitable form, such as discrete particles, dispersions, solutions and/or flakes (e.g., aluminum flakes). A single colorant or a mixture of two or more colorants can be used in the coating composition described herein.

[0034] 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.

[0035] Example pigments and/or pigment compositions include, but are not limited to, carbazole dioxazine crude pigment, azo, monoazo, disazo, naphthol AS, salt type (lakes), benzimidazolone, condensation, metal complex, isoindolinone, isoindoline and polycyclic phthalocyanine, quinacridone, perylene, perinone, diketopyrrolo pyrrole, thioindigo, anthraquinone, indanthrone, anthrapyrimidine, flavanthrone, pyranthrone, anthanthrone, dioxazine, triarylcarbonium, 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.

[0036] 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.

[0037] 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 MAXITONER INDUSTRIAL COLORANTS commercially available from Accurate Dispersions division of Eastman Chemical, Inc.

[0038] 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. Patent 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-agglomeration of nanoparticles within the coating, a dispersion of resin-coated nanoparticles can be used. As used herein, a "dispersion of resin-coated nanoparticles" refers to a continuous phase in which discreet "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 United States Patent Application Publication 2005-0287348, filed June 24, 2004, U.S. Provisional Application No. 60/482,167 filed June 24, 2003, and United States Patent Application Serial No. 11/337,062, filed January 20, 2006, which is also incorporated herein by reference.

[0039] Example special effect compositions that may be used include pigments and/or compositions that produce one or more appearance effects such as reflectance, pearlescence, metallic sheen, phosphorescence, fluorescence, photochromism, photosensitivity, thermochromism, goniochromism and/or color-change. Additional special effect compositions can provide other perceptible properties, such as opacity or texture. In a non-limiting embodiment, special effect compositions can produce a color shift, such that the color of the coating changes when the coating is viewed at different angles. Example color effect compositions are identified in U.S. Patent 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.

[0040] 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.

[0041] In a non-limiting embodiment, the photosensitive composition and/or photochromic composition can be associated with and/or at least partially bound to, such as by covalent bonding, a polymer and/or polymeric materials of a polymerizable component. In contrast to some coatings in which the photosensitive composition may migrate out of the coating and crystallize into the substrate, the photosensitive composition and/or photochromic composition associated with and/or at least partially bound to a polymer and/or polymerizable component in accordance with a non-limiting embodiment of the present invention, have minimal migration out of the coating. Example photosensitive compositions and/or photochromic compositions and methods for making them are identified in U.S. Application Serial No. 10/892,919, filed July 16, 2004.

[0042] 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.

[0043] 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.

[0044] 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.

[0045] 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.

[0046] 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.

[0047] The coating compositions may be cured using any technique known in the art such as, without limitation, thermal energy, infrared, ionizing or actinic radiation, or by any combination thereof. In certain embodiments, the curing operation can be carried out at temperatures $\geq 10^{\circ}\text{C}$. In other embodiments, the curing operation can be carried out at

temperature $\leq 246^{\circ}\text{C}$. 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 - 150°C . It should be noted, however, that lower or higher temperatures may be used as necessary to activate the curing mechanisms.

[0048] 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 .

[0049] The dry film thickness of the coating layers described herein can range from 0.1 micron to 500 microns. In other embodiments, the dry film thickness can be ≤ 125 microns, such as ≤ 80 microns. For example, the dry film thickness can range from 15 microns to 60 microns.

[0050] While specific embodiments of the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular arrangements disclosed are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the full breadth of the claims appended and any and all equivalents thereof.

Examples

Example A

[0051] **Cationic Resin A:** A cationic resin was prepared from a mixture of the following ingredients:

1039.8g of crosslinker 1 (see description below), 55.0g of Macol 98 B (Bisphenol A-6 ethylene oxide polyol available from BASF Corporation), 69.6g of diethylene glycol mono butyl ether formal, 528.7g Epon 828 (Epoxy resin available from Resolution Performance Products), 203.9g bisphenol A, and 0.18g Tetronic 150R1 (Available from BASF Corporation), are charged to a 4 neck round bottom flask, fit with a stirrer, temperature measuring probe, N_2 blanket and Dean-Stark trap. The mixture is heated to 75°C and 34.7g of diethanolamine is added. The mixture exotherms to $\sim 80^{\circ}\text{C}$ and is held for 30 minutes after the addition of the diethanolamine. 80.3g of aminopropyl diethanolamine is added, the

temperature is adjusted to 132°C and the mixture is then held at this temperature for 2 hours while collecting approximately 30g of solvent in the Dean-Stark trap. 1680g of this mixture is poured into a mixture of 30.5g sulfamic acid, 1181g deionized water, 1.15g 88% lactic acid and 66.3g of additive resin 1 (description below). The mixture is stirred for 30 minutes. 1183g of deionized water is added and mixed in well. 1000g of deionized water is added and mixed in well. Solvent and water are removed by vacuum distillation, the solids of the resulting aqueous dispersion is adjusted to 39 %. The methylisobutyl ketone content of the dispersion is less than 0.2%.

[0052] Crosslinker 1 is prepared by adding 1320 g (10 eq.) of Desmodur LS 2096 (MDI type isocyanate available from Bayer Corporation) to a mixture of 92g ethanol, 456g propylene glycol, 740g Macol 98 B (see above), and 486 g diethylene glycol mono butyl ether formal and 93g methylisobutyl ketone. 68 g of methylisobutyl ketone is used as a rinse for the isocyanate. The temperature is allowed to increase to 115°C and the mixture is held until the Infrared spectrum indicates the absence of isocyanate.

[0053] Description of additive resin 1

1	MAZEEN 355 70 ¹	1423.49
2	acetic acid	15.12
3	Dibutyltin dilaurate	1.52
4	Toluene diisocyanate 80/20	200.50
5	sulfamic acid	79.73
6	deionized H ₂ O	1623.68
7	deionized H ₂ O	766.89

¹ Amine functional diol of amine equivalent weight 1131 available from BASF Corporation

[0054] Items 1 and 2 are charged to a 4 neck round bottom flask, fit with a stirrer, temperature measuring probe and N₂ blanket and mixed for 10 minutes. Item 3 is added and then Item 4 is charged over about 1 hour allowing the reaction mixture to exotherm to a maximum temperature of 100°C. The mixture is then held at 100°C until the Infrared spectrum indicates the absence of isocyanate (approximately 1 hour). 1395 g of the reaction mixture is poured into a mixture of items 5 and 6 and mixed for 1 hour. Item 7 is then added over about 1 hour and mixed for about 1 hour. The resulting aqueous solution had a solids content of about 36%.

Example B

[0055] Cationic Resin B: A cationic resin was prepared from a mixture of the following ingredients:

	Material	Weight (grams)
1	butyl Carbitol formal ¹	81.2

	2	epon 828 ²	755.3	
	3	bisphenol A	317.3	
	4	tetronic 150R1 ³	0.23	
	5	aminopropyldiethanolamine ⁴	91.8	
1	6	diethanolamine	59.5	Available from BASF Corp. as
Mazon 1651	7	monoethanolamine	5.76	Epoxy resin available from Hexlon
2	8	Methyl isobutyl ketone (mibk)	10.1	Chemicals
Specialty	9	methoxypropanol	30.2	Available from BASF Corp.
3	10	epon 828	23.8	Available from Air Products Corp.
4	11	Blocked isocyanate		Reaction product of 10 equivalents
5		crosslinker ⁵	1083	U.S. 2088 (Bayer Corp.) with
of Desmodur				silanol, 7 moles propylene
2 moles of				mole of Macol 98B (bisphenol
glycol and 1				adduct of molecular weight 500,
ethylene oxide				BASF Corp.) as a
		Solubilization (g resin)	2040	
	12	Sulfamic Acid	89	
	13	Deionized water	3683	
[0056]	14	Yttrium trioxide	18.5	Procedure: Items 1, 2, 3,
and 4 are	15	Deionized water	4433	charged to a 4 neck
round			10264	bottom flask, fit with a

stirrer, temperature measuring probe, N₂ blanket and Dean-Stark trap and heated to 70°C and held with mixing for 15 minutes. Heating was stopped and items 5, 6 and 7 (mixed) were added. The reaction mixture exotherms to a maximum of 176°C after about 10 minutes. Items 8 and 9 (mixed) are added slowly 15 minutes after the peak exotherm temperature and the mixture is allowed to cool to 145°C and held at this temperature for a total of 2 hours from the peak exotherm temperature. Items 10 and 11 are then added and the mixture is adjusted to 110°C. 2040g of the reaction mixture are poured with vigorous agitation into a solution of items 12, 13 and 14 which was previously prepared by heating and stirring the mixture of 12, 13, and 14 to 60°C for 30 minutes, then cooling to 50°C. The resin dispersion is mixed for about 1 hour. Item 15 is added slowly with stirring. The final aqueous dispersion had a measured solids content of 20 %.

Example C

[0057] Grind Resin: This example describes the preparation of a quaternary ammonium salt containing pigment-grinding resin. Example C-1 describes the preparation of an amine-acid salt quaternizing agent and Example C-2 describes the preparation of an epoxy group-containing polymer that is subsequently quaternized with the amine-acid salt of Example C-1.

[0058] C-1 The amine-acid salt quaternizing agent was prepared using the following procedure:

#	Material	Parts
1	Dimethyl ethanolamine	445
2	PAPI 290 available from Dow Chemical Co.	660
3	Butyl Carbitol Formal available from BASF Corp.	22.1
4	88% lactic acid aqueous	512
5	DI water	2136.11

[0059] Material 1 was charged in a suitably equipped 5 liter flask. Material 2 was then charged under mild agitation over a 1.5 hour period, followed by a rinse of material 3. During this addition, the reaction mixture was allowed to exotherm to a temperature of about 89° C. and held at that temperature for about 1 hour until complete reaction of the Isocyanate as determined by infrared spectroscopy. At that time, material 4 was added over a 25 minute period, followed material 5. The reaction temperature was held at about 80° C. for about 6 hours until a stalled acid value of 70.6 was obtained.

[0060] C-2 The quaternary ammonium salt group-containing polymer was prepared using the following procedure.

#	Material	Parts
1	Bisphenol A Diglycidyl ether available from Resolution Chemical Co. as Epon 828	528.8
2	Bisphenol A	224.9
3	Butyl Carbitol Formal	83.7
4	ethyltriphenylphosphonium iodide	0.5
5	Butyl Carbitol Formal	164.9
6	amine-acid quaternizing agent of B-1	418.4
7	DI water	1428.1
8	Butyl Carbitol Formal	334.7

[0061] Material 1 was charged to a suitably equipped 5 liter flask under mild agitation. Material 2 was then added followed by material 3 and material 4. The reaction mixture was

heated to about 140° C., allowed to exotherm to about 180° C., then cooled to about 160° C. and held at that temperature for about 1 hour. At that time the polymeric product had an epoxy equivalent weight of 982.9. The reaction mixture was then cooled to a temperature of about 130° C. at which time material 5 was added and the temperature lowered to about 95°-100° C., followed by the addition of material 6, the amine-acid quaternizing agent of 6-1 over a period of 15 minutes, and subsequently followed by the addition of about 1428.1 parts by weight of deionized water. The reaction temperature was held at about 80° C. for approximately 6 hours until the acid number of the reaction product fell below 1.0. The resultant quaternary ammonium salt group-containing pigment grinding resin was further reduced with about 334.7 parts by weight of the solvent of Butyl Carbitol Formal.

Example D

[0062] **Pigment Paste:** This example describes the preparation of a pigment paste suitable for use in the electrodeposition bath compositions of the present invention.

[0063] The pigment paste was prepared with the following ingredients:

Weight (grams)	Material
988.1	Quaternary ammonium salt group containing grind resin of Example C
518.2	Catalyst paste ¹
50.3	Surfynol GA surfactant from Air Products & Chemicals Inc.
24.4	Ethylene Glycol Monohexylether from BASF Corp.
24.4	N-Butoxypropanol from Dow Chemical Co.
13.0	Carbon black available from Printex 200
389.0	Aluminum silicate clay available from BASF Catalysts LLC
727.8	Titanium Dioxide from Tronox Inc.
265.0	DI water

¹ Prepared from a mixture of the following ingredients: 632 grams: Quaternary ammonium salt group containing grind resin of Example C; 92 grams of DI water; 19 grams of n-Butoxypropanol; and 368 grams of STANN BO (Di-n-butyltin oxide catalyst available from Sankyo Organic Chemicals Co., Ltd.). The above ingredients were added in the order shown under high shear agitation. After ingredients were thoroughly blended, the pigment paste was transferred to a vertical sand mill and ground to a Hegman value of about 7.25.

[0064] The above ingredients were first dispersed with a high speed cowles blade for 30 minutes, and then milled in a Premier Mill with 1.0-1.6mm Zircoa media for 1 hour or until Hegman value reaches about 7.

Example E

[0065] Resin Blend 1: This example describes the preparation of a master batch of the resin blend that was used in the Paints 1, 3, and 5 below.

Weight (grams)	Material
2349.0	Cationic resin from Example A
246.9	Flexiblizer ¹
32.4	Plasticizer ²
12.0	Propylene Glycol monomethyl ether from BASF Corp.
6.0	Ethylene Glycol Monoheylether from BASF Corp.
120.0	Flow additive ³
233.7	DI water

¹ 711g of DER732 (Aliphatic epoxy resin available from Dow Chemical Co.) and 164.5g bisphenol A are charged to a suitably equipped 3-liter round-bottomed flask. The mixture is heated to 130°C and 1.65g benzyldimethyl amine is added. The reaction mixture is held at 135°C until the epoxide equivalent weight of the mixture is 1232. 78.8g of butyl Carbitol formal (Available as Mazon 1651 from BASF Corporation) is added and then the mixture is cooled to 95°C. 184.7g Jeffamine D400 (Polyoxypropylene diamine available from Huntsman Corp.) is added and the reaction held at 95°C until the Gardner-Holdt viscosity of a sample of the resin diluted 50/50 in methoxy propanol is "H". A mixture of 19.1g Epon 828 and 3.4g butyl Carbitol formal is added and the mixture held until the Gardner-Holdt viscosity of a sample of the resin diluted 50/50 in methoxy propanol is "Q". 388.8g of this resin is poured into a mixture of 1242.13g deionized water and 30.2g sulfamic acid and mixed for 30 minutes. 614.8g deionized water is then added and mixed well. The final aqueous dispersion had a measured solids content of 35.8%.

² Reaction product of 2 moles of diethylene glycol monobutyl ether and 1 mole formaldehyde, 98% active, prepared as described in U.S. Pat. No. 4,891,111 to McCollum et al.

³ Prepared by a process comprising mixing a cationic polyepoxideamine reaction product and a polyepoxide crosslinking agent as described in U.S. Pat. No. 5,096,956 to Corrigan et al.

Example F

[0066] Resin Blend 2: This example describes the preparation the resin blend that was used in Paint 7 below:

Weight (grams)	Material
1820.0	Cationic resin from Ex. B
67.1	Flexiblizer that is described in Ex. E
11.7	Plasticizer that is described in Ex. E
4.3	Propylene Glycol monomethyl ether from BASF Corp.

2.2	Ethylene Glycol Monohexylether from BASF Corp.
43.5	Flow additive that is described in Ex. E
103.5	DI water

Example AA

[0067] Yttrium Solution: This example describes the preparation of a soluble yttrium solution for use in the electrodeposition bath compositions of Paints 2, 4, and 6 in Table 1. The soluble yttrium solution was prepared from a mixture of the following:

Weight (grams)	Material
112.9	Yttrium Trioxide
485.0	DI water
291.3	Sulfamic Acid

[0068] To a suitably equipped 5 liter flask add sulfamic acid and water and stir for 20 minutes. Heat solution to 98 °C and then hold until a clear solution is obtained. Hold for at least 2 hours. Allow solution to cool below 50 °C.

Example BB

[0069] Silane Solution 1: This example describes the preparation of an amino silane solution that is suitable for use in the electrodeposition bath compositions of Paints 3, 4, and 7 in Table 1.

Weight (grams)	Material
150.0	DI water
30.2	Aminopropylsilsesquioxane from Gelest, Inc. as WSA-9911

[0070] Combine the above ingredients and allow to mix for 20 minutes. After 20 minutes, add 88% lactic acid until pH reaches about 5.5.

Example CC

[0071] Silane Solution 2: This example describes the preparation of mixture of Bis (trimethoxysilylpropyl)amine and vinyltriacetoxysilane that is suitable for use in the electrodeposition bath compositions of Paints 5 and 6.

Weight (grams)	Material
40.0	Bis (trimethoxysilylpropyl)amine available from GE Silicones as Silquest A-1170
8.0	Vinyltriacetoxysilane available from Gelest, Inc.

[0072] Combine the above ingredients and allow to mix for 20 minutes.

[0073] The following table provides the preparation of electrodeposition bath compositions of the invention:

[0074] Table I:

Paint	Resin Blend (grams) from Ex. E	Resin Blend (grams) from Ex. F	Pigment Paste (grams) from Ex. D	DI Water (grams)	Yttrium Soln. (grams) from Ex. AA	Silane Soln. 1 (grams) from Ex. BB	Silane Soln. 2 (grams) from Ex. CC	UF %
1	1086.7	0	136.1	977.2	0	0	0	30
2	0	0	0	20.0	11	0	0	0
3	1063.6	0	136.1	834.3	0	166	0	30
4	0	0	0	20.0	11	0	0	0
5	1063.6	0	136.1	992.0	0	0	8.3	30
6	0	0	0	20.0	11	0	0	0
7	0	1948.8	133.9	103.5	0	8.3	0	30

[0075] Paints 1, 3, and 5 were made by adding the cationic resin blend from Example E into a 1 gallon plastic container. The pigment paste is then diluted with about 200 grams of the DI water before adding it to the resin blend. If noted in the table above, the silane solution was diluted with about 20 grams of DI water prior to addition. The remaining DI water is then added to the container. Final bath solids were about 21.5% , with a pigment to binder ratio of about 0.14. The test baths were ultrafiltered 30% and replenished with only fresh DI water. After ultrafiltration, paints 2,4, and 6 were made by post adding the amounts listed in the table above of DI water, yttrium and/or silane to paints 1, 3, and 5 respectively.

[0076] Paint 7 was made by adding the cationic resin blend from Example F into a 1 gallon plastic container. The pigment paste is then diluted with about 50 grams of DI water and added to the resin blend. The silane solution from example BB is diluted with the remaining DI water and added to the mixture.

[0077] The above paint compositions in examples (2) through (7) were compared to example (1). The test substrate was 4"x6" ACT CRS and EZG panels that were cleaned with an alkaline cleaner. The panels were not pretreated prior to electrocoating. These panels are available from ACT Laboratories of Hillside, Michigan.

[0078] Each of the electrodeposition bath compositions of examples 1 through 7 were electrodeposited onto non-phosphated cold rolled and electrogalvanized steel panels. Conditions for cationic electrodepositions of each were as follows: 20-70 columbs, 150-200 volts, at 92°F to yield a cured film thickness of 0.8-1.0 mils. The coated substrate was cured in an electric oven at 350°F for 20 minutes.

[0079] Each of the coated untreated steel test panels was subjected to adhesion testing using an Elcometer PATTI 110 adhesion tester. The results that are reported on the following table are for test panels that have been subjected to 16 hours of condensing humidity.

[0080] Table 2:

PATTI Adhesion (post QCT) burst pressure (psi)				
Paint	CRS	EZG	Silane Added	Yttrium Added from Ex. AA
1	335	250	NONE	NONE
2	382	264	NONE	YES
3	303	390	From Ex BB	NONE
4	746	790	From Ex BB	YES
5	399	302	From Ex CC	NONE
6	842	750	From Ex CC	YES
7	448	778	From Ex BB	YES

[0081] The data reported in table 2 illustrates the improvement in post-QCT PATTI adhesion when a silane and soluble yttrium salts are present in the electrodeposition baths of the invention.

What is claimed:

1. An electrodepositable coating composition comprising (i) an electrodepositable film-forming polymer, (ii) a corrosion inhibitor, and (iii) a solution of a silane that does not contain an ethylenically unsaturated double bond.
2. The electrodepositable coating composition according to claim 1, wherein the corrosion inhibitor comprises a rare earth metal, a lanthanide, or combinations thereof.
3. The electrodepositable coating composition according to claim 2, wherein the corrosion inhibitor is yttrium.
4. The electrodepositable coating composition according to claim 1, wherein the (ii) corrosion inhibitor comprises ≤ 5 weight % of the total resin solids of the electrodepositable coating composition.
5. The electrodepositable coating composition according to claim 1, wherein the (iii) silane comprises ≤ 5 weight % of the total resin solids of the electrodepositable coating composition.
6. The electrodepositable coating composition according to claim 1, wherein the electrodepositable coating composition further comprises a silane that contains an ethylenically unsaturated double bond.
7. The electrodepositable coating composition according to claim 1, wherein the silane comprises a functional group, and wherein the functional group comprises amino, epoxy, thiol, or combinations thereof.
8. The electrodepositable coating composition according to claim 1, wherein the electrodepositable coating composition further comprises bismuth, copper, zinc, silver, zirconium, or combinations thereof.
9. The electrodepositable coating composition according to claim 1, wherein (i) the electrodepositable film-forming polymer comprises reactive functional groups and wherein the electrodepositable coating composition further comprises (iv) a crosslinking agent that is reactive with the reactive functional groups of component (i).
10. The electrodepositable coating composition according to claim 9, wherein the electrodepositable coating composition further comprises a curing catalyst.
11. The electrodepositable coating composition according to claim 10, wherein the curing catalyst comprises an organotin compound, bicyclic guanidine, or combinations thereof.
12. A substrate coated with the electrodepositable coating composition of claim 1.
13. The substrate according to claim 12, wherein said substrate is not pretreated with a phosphate or zirconium pretreatment solution prior to coating the substrate with the electrodepositable coating composition.

14. The substrate according to claim 12, wherein said substrate is pretreated with a phosphate or a zirconium pretreatment solution prior to coating the substrate with the electrodepositable coating composition.
15. The substrate according to claim 12, wherein said substrate comprises steel, galvanized steel, or aluminum.
16. The electrodepositable coating composition according to claim 1, wherein the silane is an aminosilane.
17. An electrodepositable coating composition consisting essentially of (i) an electrodepositable film-forming polymer comprising reactive functional groups, (ii) yttrium, (iii) a solution of a silane that does not contain an ethylenically unsaturated double bond; (iv) a crosslinking agent that is reactive with the reactive functional groups of the film forming polymer; and (v) a catalyst.
18. The electrodepositable coating composition according to claim 17, wherein after application to a substrate and after curing, demonstrates a burst pressure, when subjected to the PATTI ADHESION TEST, which is at least 100 psi greater than the burst pressure of an electrodepositable coating composition comprising the film-forming polymer that does not contain (ii) yttrium and a (iii) silane.
19. The electrodepositable coating composition according to claim 17, wherein the silane comprises a functional group, and wherein the functional group comprises amino, epoxy, thiol, or combinations thereof.
20. An electrodepositable coating composition comprising (i) an electrodepositable film-forming polymer, (ii) yttrium, and (iii) a solution of an aminosilane.
21. The electrodepositable coating composition according to claim 20, wherein the aminosilane comprises a functional group comprising an ethylenically unsaturated double bond, hydroxyl, carbamate, epoxy, isocyanate, amine-salt, mercaptan, or combinations thereof.
22. The electrodepositable coating composition according to claim 20, wherein after application to a substrate and after curing, demonstrates a burst pressure, when subjected to the PATTI ADHESION TEST, which is at least 100 psi greater than the burst pressure of an electrodepositable coating composition comprising the film-forming polymer that does not contain (ii) yttrium and a (iii) silane.
23. The electrodepositable coating composition according to claim 20, wherein (i) the electrodepositable film forming polymer comprises reactive functional groups and wherein the electrodepositable coating composition further comprises (iv) a crosslinking agent that is reactive with the reactive functional groups of component (i).

24. The electrodepositable coating composition according to claim 23, wherein the electrodepositable coating composition further comprises (v) a catalyst.
25. The electrodepositable coating composition according to claim 24, wherein the catalyst comprises dibutyl tin oxide, bicyclic guanidine, or combinations thereof.
26. A substrate coated with the electrodepositable coating composition of claim 20.