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(71) Applicant: **PPG INDUSTRIES OHIO, INC.** [US/US]; 3800 West 143rd Street, Cleveland, Ohio 44111 (US).

(72) Inventors: **MCMILLEN, Mark W.**; 447 Fisher Road, Cabot, Pennsylvania 16023 (US). **LEMON, Steven J.**; 275 Fairview Drive, Lower Burrell, Pennsylvania 15068 (US). **VOTRUBA-DRZAL, Peter L.**; 119 Yorkshire Drive, Pittsburgh, Pennsylvania 15208 (US). **KARABIN, Richard F.**; 107 Karabin Lane, Ruffs Dale, Pennsylvania 15679 (US).

(74) Agent: **MEYERS, Diane R.** et al.; PPG Industries, Inc., One PPG Place, 39th Floor, Pittsburgh, Pennsylvania 15272 (US).

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(54) Title: SYSTEM FOR NICKEL-FREE ZINC PHOSPHATE PRETREATMENT

(57) Abstract: Disclosed is a substrate pretreatment system, comprising (a) an activating rinse for treating at least a portion of a substrate comprising a dispersion of metal phosphate particles having a D_{90} particle size of no greater than 10 µm, wherein the metal phosphate comprises divalent or trivalent metals or combinations thereof; and (b) a pretreatment composition for treating at least a portion of the substrate treated with the activating rinse, comprising zinc ions and phosphate ions, wherein the pretreatment composition is substantially free of nickel. Methods of treating a substrate with the substrate pretreatment system also are disclosed. Substrates treated with the substrate pretreatment system also are disclosed.

SYSTEM FOR NICKEL-FREE ZINC PHOSPHATE PRETREATMENT

FIELD OF THE INVENTION

[0001] A system for pretreating a substrate with a nickel-free zinc phosphate pretreatment composition is disclosed.

BACKGROUND

[0002] Phosphate conversion coatings are well known for treating metal surfaces, particularly ferrous, zinc and aluminum metals and their alloys. When applied, these phosphate coatings form a phosphate layer, primarily of zinc and iron phosphate crystals, which provides corrosion resistance and/or enhances the adhesion of subsequently applied coatings.

[0003] Prior to application of the phosphate coating, the metal substrate is typically “conditioned” or “activated” by subjecting the surface of the metal substrate to a diluted aqueous dispersion, sometimes referred to as an activating rinse or activator, by introducing or immersing the metal substrate into a tank that contains the activating rinse. “Activation” of the surface of the metal substrate often is achieved due to the adsorption of colloidal titanium-phosphate particles, which are present in the activating rinse, to the metal’s surface. These colloidal titanium-phosphate particles, however, have a tendency to agglomerate in the activating rinse bath due to dissolved cations that are typically present in the activating rinse conditioner bath.

[0004] The phosphate conversion coating is typically applied to a substrate by immersing the substrate into a heated bath comprising metal phosphate particles.

[0005] Conventional techniques for coating such substrates include techniques that involve pretreating the metal substrate with nickel-containing compositions. The use of such nickel-containing compositions, however, impart environmental concerns.

SUMMARY

[0006] Disclosed is a substrate pretreatment system, comprising (a) an activating rinse for treating at least a portion of a substrate comprising a dispersion of metal phosphate particles having a D_{90} particle size of no greater than 10 μm, wherein the metal phosphate comprises divalent or trivalent metals or combinations thereof; and (b) a pretreatment composition for treating at least a portion of the substrate treated with the activating rinse, comprising zinc ions and phosphate ions, wherein the pretreatment composition is substantially free of nickel.

[0007] Also disclosed is a method of treating a substrate with the substrate pretreatment system.

[0008] Also disclosed is a substrate treated with the substrate pretreatment system.

DETAILED DESCRIPTION

[0009] According to the present invention, the substrate pretreatment system comprises, or in some instances consists of, or in some instances consists essentially of: an activating rinse for treating at least a portion of a substrate comprising a dispersion of metal phosphate particles having a D_{90} particle size of no greater than 10 μm, wherein the metal phosphate comprises divalent or trivalent metals or combinations thereof; and (b) a pretreatment composition for treating at least a portion of the substrate treated with the activating rinse, comprising zinc ions and phosphate ions, wherein the pretreatment composition is substantially free of nickel.

[0010] As used herein, the phrase “activating rinse” refers to a continuous aqueous medium having dispersed and/or suspended therein metal phosphate particles that is applied onto at least a portion of a substrate and/or into which at least a portion of a substrate is immersed to “activate” or “condition” the substrate in order to promote the formation of a metal phosphate coating on at least a portion of the substrate that was treated with the activating rinse. As used herein, to “activate” or “condition” the substrate surface means to create nucleation sites on the substrate surface. While not wishing to be bound by theory, it is believed that such nucleation sites promote the formation of metal phosphate crystals on the substrate surface when the substrate surface subsequently is treated with a metal phosphate pretreatment composition. For example, activation of the substrate surface is believed to create nucleation sites that promote the formation of zinc and zinc/iron phosphate crystals on the substrate surface when the substrate surface is pretreated with a zinc phosphate pretreatment composition.

[0011] Non-limiting examples of a suitable substrate that can be treated with the activating rinse include, but are not limited to, a metal and/or a metal alloy substrate. For example, the metal and/or metal alloy can comprise or be aluminum, steel, or zinc. According to the present invention, a steel substrate could include cold rolled steel, electrogalvanized steel, and hot dipped galvanized steel. According to the present invention, 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.

[0012] As used herein, the term “vehicle” or variations thereof includes, but is not limited to, civilian, commercial, and military land vehicles such as cars and trucks.

[0013] As used herein, the term "dispersion" refers to a two-phase transparent, translucent or opaque system in which metal phosphate particles are in the dispersed phase and an aqueous medium, which includes water, is in the continuous phase. An “aqueous medium” is a liquid medium that is 50 weight percent or greater of water, with weight percent based on non-solid content of the activating rinse. The aqueous medium may comprise 50 weight percent or less of other organic co-solvents, such as 10 weight percent or less. According to the present invention, the organic co-solvents are at least partially miscible with water. In the aqueous medium, water miscible organic solvents may be present, for example, alcohols with up to about 8 carbon atoms such as methanol, isopropanol, and the like, or glycol ethers such as the monoalkyl ethers of ethylene glycol, diethylene glycol, or propylene glycol, and the like.

[0014] As used herein, the term “pulverized” refers to particles having variable aspect ratios, where the term “aspect ratio” refers to the ratio of the length to the width of a particle (i.e., the aspect ratio does not define a sphere).

[0015] According to the present invention, the metal phosphate particles of the dispersion of metal phosphate particles of divalent or trivalent metals or combinations thereof may have a D_{90} particle size that is not greater than 10 μm, such as not greater than 8 μm, such as not greater than 5 μm, such as not greater than 2 μm, such as not greater than 1 μm and in some cases may be at least 0.06 μm, such as at least 0.1 μm, such as at least 0.2 μm. According to the present invention, the metal phosphate particles of the dispersion of phosphate particles of divalent or trivalent metals or combinations thereof may have a D_{90} particle size of 0.06 μm to 8 μm, such as 0.1 μm to 5 μm, such as 0.2 μm to 2 μm.

[0016] As used herein, the term “D_{90}” particle size refers to a volume-weighted particle distribution in which 90% of the particles in the particle distribution have a diameter smaller than the “D_{90}” value. As used herein, the term “D_{10}” particle size refers to a volume-weighted particle distribution in which 10% of the particles in the particle distribution have a diameter smaller than the “D_{10}” value. As used herein, the term “D_{50}” particle size refers to a volume-weighted particle distribution in which 50% of the particles in the particle distribution have a diameter smaller than the “D_{50}” value.

[0017] According to the present invention, particle size may be measured using an instrument such as a Mastersizer 2000, available from Malvern Instruments, Ltd., of Malvern, Worcestershire, UK, or an equivalent instrument. The Mastersizer 2000 directs a laser beam (0.633 mm diameter, 633 nm wavelength) through a dispersion of particles (in distilled, deionized or filtered water to 2-3% obscuration), and measures the light scattering of the dispersion (measurement parameters 25°C, 2200 RPM, 30 sec premeasurement delay, 10 sec background measurement, 10 sec sample measurement). The amount of light scattered by the dispersion is inversely proportional to the particle size. A series of detectors measure the scattered light and the data are then analyzed by computer software (Malvern Mastersizer 2000 software, version 5.60) to generate a particle size distribution, from which particle size can be routinely determined.

[0018] According to the present invention, the sample of dispersion of particles optionally may be sonicated prior to analysis for particle size. According to the present invention, the sonication process comprises: (1) mixing the dispersion of particles using a Vortex mixer (Fisher Scientific Vortex Genie 2, or equivalent); (2) adding 15 mL of distilled deionized, ultra-filtered water to a 20 mL screw-cap scintillation vial; (3) adding 4 drops of the dispersion to the vial; (4) mixing the contents of the vial using the Vortex mixer; (5) capping the vial and placing it into an ultrasonic water bath (Fisher Scientific Model FS30, or equivalent) for 5 minutes; (6) vortexing the vial again; and (7) adding the sample dropwise to the Mastersizer to reach an obscuration between 2-3 for particle size distribution analysis described above.

[0019] According to the present invention, the metal phosphate particles may be substantially pulverized, such that more than 90% of the metal phosphate particles in the activating rinse composition are pulverized, such as more than 91%, such as more than 92%, such as more than 93%, such as more than 94%, such as more than 95%, such as more than 96%, such as more than 97%, such as more than 98%, such as more than 99%. According to the present invention, the metal phosphate particles may be completely pulverized, such that 100% of the particles are pulverized.

[0020] According to the present invention, the metal phosphate (as total metal compound) may be present in the activating rinse in an amount of at least 50 ppm, based on total weight of the activating rinse, such as at least 150 ppm, and in some instances may be present in the activating rinse in an amount of no more than 5000 ppm, based on total weight of the activating rinse, such as no more than 1500 ppm. According to the present invention, the metal phosphate (as total metal compound) may be present in the activating rinse in an amount of 50 ppm to 5,000 ppm of total metal phosphate based on the total weight of the activating rinse, such as of 150 ppm to 1,500 ppm.

[0021] According to the present invention, the divalent or trivalent metal of the metal phosphate may comprise zinc, iron, calcium, manganese, aluminum, nickel, or combinations thereof. If combinations of different metal phosphates are employed, they may comprise the same or different metals, and may be selected from the particular zinc, iron, calcium, manganese and aluminum phosphates mentioned in the following.

[0022] Suitable zinc phosphates useful in the activating rinse bath include, without limitation $Zn_3(PO_4)_2$, $Zn_2Fe(PO_4)_2$, $Zn_2Ca(PO_4)_2$, $Zn_2Mn(PO_4)_2$, or combinations thereof.

[0023] Suitable iron phosphates useful in the activating rinse bath include, without limitation $FePO_4$, $Fe_3(PO_4)_2$, or combinations thereof.

[0024] Suitable calcium phosphates useful in the activating rinse bath include, without limitation $CaHPO_4$, $Ca_3(PO_4)_2$, or combinations thereof.

[0025] Suitable manganese phosphates useful in the activating rinse bath include, without limitation $Mn_3(PO_4)_2$, $MnPO_4$, or combinations thereof.

[0026] Suitable aluminum phosphates useful in the activating rinse bath include, without limitation $AlPO_4$.

[0027] According to the present invention, the activating rinse may further comprise a dispersant. The dispersant may be ionic or non-ionic. Suitable ionic dispersants useful in the activating rinse may comprise an aromatic organic acid, a phenolic compound, a phenolic resin, or combinations thereof. Suitable non-ionic dispersants useful in the activating rinse may include non-ionic polymers, in particular those comprised of monomers (or residues thereof) including propylene oxide, ethylene oxide, styrene, a monoacid such as (meth)acrylic acid, a diacid such as maleic acid or itaconic acid, an acid anhydride such as acrylic anhydride or maleic anhydride, or combinations thereof. Examples of suitable commercially available non-ionic dispersants include DISPERBYK®-190 available from BYK-Chemie GmbH and ZetaSperse® 3100 available from Air Products Chemicals Inc.

[0028] According to the present invention, the activating rinse may be substantially free or completely free of ionic dispersants. As used herein, an activating rinse is substantially free of ionic dispersants if ionic dispersants are present in an amount less than 1% by weight, based on the total weight of the activating rinse. As used herein, an activating rinse is completely free of ionic dispersants if ionic dispersants are not present in the activating rinse, meaning 0% by weight based on the total weight of the activating rinse.

[0029] According to the present invention, the activating rinse optionally may include a metal sulfate salt. The metal of the metal sulfate may be the same as or different from the metal of the metal phosphate particles. According to the present invention, the metal of the metal sulfate salt may comprise a divalent metal, a trivalent metal or combinations thereof, such as, for example, nickel, copper, zinc, iron, magnesium, cobalt, aluminum or combinations thereof.

[0030] According to the present invention, when present, if at all, the sulfate ion of the metal sulfate salt may be present in the activating rinse in an amount of at least 5 ppm based on the total weight of the activating rinse, such as at least 10 ppm, such as at least 20 ppm, such as at least 50 ppm, and in some cases, no more than the solubility limit of the metal sulfate salt in the activating rinse, such as no more than 5,000 ppm, such as no more than 1,000 ppm, such as no more than 500 ppm, such as no more than 250 ppm. According to the present invention, the sulfate ion of the metal sulfate salt may be present in an amount of 5 ppm to 5,000 ppm based on a total amount of sulfate in the metal sulfate salt, such as 10 ppm to 1,000 ppm, such as 20 ppm to 500 ppm, such as 50 ppm to 250 ppm. According to the present invention, the activating rinse may be substantially free, or in some instances, completely free, of sulfate ions. As used herein with respect to the sulfate ion of a metal sulfate salt, the term “substantially free” means that the sulfate ion is present in the activating rinse in an amount of less than 5 ppm based on the total weight of the activating rinse. As used herein with respect to the sulfate ion of a metal sulfate salt, the term “completely free” means that the activating rinse does not comprise a sulfate ion (i.e., there are 0 ppm of sulfate ion (based on the total weight of the activating rinse) present in the activating rinse).

[0031] According to the present invention, the activating rinse may be in the form of a concentrate, wherein the concentrate has a viscosity sufficient to prevent the metal phosphate particles and metal sulfate salt (if present) from settling out. According to the present invention, in use, the concentrated activating rinse may be diluted with water and/or an organic solvent.

[0032] According to the present invention, the activating rinse may be a 1K ("One-Component", or "One Part") composition or a multi-component composition, such as, for example, 2K ("Two-Component", or 'Two Part") compositions. As defined herein, a "1K" composition is a composition in which all of the ingredients may be premixed and stored. By contrast, a multi-component composition is one in which at least two of the ingredients are stored separately and are mixed together to form the treatment bath.

[0033] According to the present invention, the activating rinse may be a 1K composition, wherein the 1K composition is formed from: a dispersion of metal phosphate particles of divalent metals, trivalent metals or combinations thereof, the metal phosphate particles having a D_{90} particle size that is not greater than 10 μm; a dispersant; and a metal sulfate salt (if present). Optionally, the 1K activating rinse may be a concentrate that is diluted to form the bath containing the activating rinse.

[0034] According to the present invention, the activating rinse may be a 2K composition wherein a dispersion of metal phosphate particles of divalent metals, trivalent metals or combinations thereof, the metal phosphate particles having a D_{90} particle size that is not greater than 10 μm, and a dispersant form a part of a first component. A metal sulfate salt may form a part of a second component. Additional components comprising any of the optional ingredients described below also may be added to the bath containing the activating rinse. Any of the components of the activating rinse may be a concentrate that is diluted to form the bath containing the activating rinse.

[0035] According to the present invention, the activating rinse may include a wetting agent. According to the present invention, wetting agents may be present at amounts of up to 2 percent by weight, such as up to 0.5 percent by weight, based on the total weight of the activating rinse. In some instances, wetting agents may be present in amounts of 0.1 percent by weight to 2 percent by weight, based on total weight of the activating rinse, such as 0.3 percent by weight to 0.5 percent by weight. As used herein, a "wetting agent" reduces the surface tension at the interface between the surface of the particles of the dispersed phase and the aqueous medium to allow the aqueous medium to more evenly contact or "wet" the surface of the particles of the dispersed phase.

[0036] According to the present invention, the activating rinse may have a pH of 6 to 12, such as 6.5 to 9, such as 7.5 to 8.5, such as 7 to 8. An alkaline component may be present in the activating rinse in an amount sufficient to adjust the pH of the activating rinse. Suitable alkaline components may include, for example, sodium hydroxide, sodium carbonate, sodium tripolyphosphate, potassium orthophosphate, or combinations thereof.

[0037] According to the present invention, the activating rinse may also include a biocide. Suitable biocides include, for example, methyl chloro isothiazolinone, methyl isothiazolinone, or combinations thereof. When utilized, the biocide may be present in an amount of at least 10 ppm based on active material in the activating rinse, such as at least 20 ppm, such as at least 80 ppm, such as at least 100 ppm, and in some instances, no more than 140 ppm, such as no more than 120 ppm, such as no more than 40 ppm, such as no more than

30 ppm. According to the present invention, the biocide may be present in an amount of 10 ppm to 140 ppm based on active material, such as 10 ppm to 40 ppm, such as 20 ppm to 30 ppm, such as 80 ppm to 140 ppm, such as 100 ppm to 120 ppm. The skilled artisan will recognize that biocides may be included in the activating rinse in amounts based on manufacturer instructions.

[0038] According to the present invention, the activating rinse may further comprise silica. According to the present invention, the silica may be a precipitated silica, such as a synthetic amorphous precipitated silica. According to the present invention, the silica may be friable under shear. As used herein, “friable under shear” means that particle size may be reduced with shear. According to the present invention, the silica may comprise, for example, Hi-Sil^{TM} EZ 160G silica (commercially available from PPG Industries, Inc.). According to the present invention, if present, the silica may be present in an amount of at least 50 ppm, based on total weight of the activating rinse, such as at least 100 ppm, such as at least 150 ppm, and in some instances, no more than 5000 ppm, based on total weight of the activating rinse, such as no more than 1000 ppm, such as no more than 500 ppm. According to the present invention, the silica may be present in the activating rinse in an amount of 50 ppm to 5,000 ppm based on the total weight of the activating rinse, such as 100 ppm to 1,000 ppm, such as from 150 ppm to 500 ppm.

[0039] The activating rinse may optionally further comprise components in addition to the dispersant (i.e., components different than the dispersant), such as nonionic surfactants and auxiliaries conventionally used in the art. Such additional optional components include surfactants that function as defoamers. Amphoteric and/or nonionic surfactants may be used. Defoaming surfactants may be present, if at all, in amounts of at least at least 0.1 percent by weight, based on total weight of the activating rinse bath, such as at least 0.5 weight percent by weight, and in some instances, may be present in amounts of no more than 1 weight percent, such as no more than 0.7 percent by weight, based on the total weight of the activating rinse bath. In some instances, defoaming surfactants may be present, if at all, in amounts of 0.1 weight percent to 1 weight percent, such as 0.5 weight percent to 0.7 percent by weight, based on total weight of the activating rinse bath.

[0040] According to the present invention, the activating rinse may further comprise a rheology modifier in addition to the dispersant (i.e., different than the dispersant). The rheology modifier may comprise, for example, polyurethanes, acrylic polymers, lattices, styrene/butadiene, polyvinylalcohols, clays such as attapulgite, bentonite, and other montmorillonite, cellulose based materials such as carboxymethyl cellulose, methyl cellulose, (hydroxypropyl)methyl cellulose or gelatin, gums such as guar and xanthan, or combinations thereof.

[0041] According to the present invention, the activating rinse may be substantially or, in some cases, completely, free of titanium-phosphate particles. As used herein, the term "substantially free," when used in reference to the absence of titanium-phosphate particles in the activating rinse, means that any titanium-phosphate particles present in the activating rinse are not purposefully added and are present in a trace amount of less than 5 ppm, based on the total weight of the activating rinse. As used herein, the term "completely free," when used in reference to the absence of titanium-phosphate particles, means that there are no titanium-phosphate particles at all.

[0042] The activating rinse of the present invention can be prepared fresh with the above-mentioned ingredients in the concentrations specified or can be prepared in the form aqueous concentrates in which the concentration of various ingredients is considerably higher such that the concentrates may be diluted with aqueous medium such as water or are diluted by feeding them into an activating bath containing an activating rinse that has been in use for some time.

[0043] According to the present invention, the activating rinse bath may comprise a chelator. The chelator may comprise, for example, carboxylates such as tartrates, citrates or gluconates, acetate based complexes such as ethylenediaminetetraacetate or nitrilotriacetate, phosphates such as pentasodium triphosphate or tetrapotassium pyrophosphate, phosphonates, polycarboxylates, the acids, esters, or salts of any of the aforementioned, or combinations thereof.

[0044] The substrate pretreatment system of the present invention also comprises a pretreatment composition comprising zinc ions and phosphate ions. The pretreatment composition may be substantially free, or in some cases, essentially free, or in some cases, completely free, of nickel. [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 and which contains phosphates of zinc, iron, and/or other divalent metals known in the art.] As used herein, the term "substantially free," when used with respect to the absence of nickel, means nickel, if present at all in the bath containing the pretreatment composition, the pretreatment composition, and/or layers formed from and comprising same, and, if present at all, only is present in a trace amount of 5 ppm or less, based on a total weight of the composition or layer(s), as the case may be. As used herein, the term "essentially free," when used with respect to the absence of nickel, means nickel, if present at all in the bath containing the pretreatment composition, the pretreatment composition, and/or layers formed from and comprising same, and, if present at all, only is present in a trace amount of 1 ppm or less, based on a total weight of the composition or layer(s), as the case may be. As used herein, the term "completely free," when used with respect to the absence of nickel, means nickel, is absent from the bath containing the pretreatment composition, the pretreatment composition, and/or layers formed from and comprising same (i.e., the bath containing the pretreatment composition, the pretreatment composition, and/or layers formed from and comprising same contain 0 ppm of nickel, excluding nickel derived from drag-in, substrate(s), and/or dissolution of equipment.

[0045] According to the present invention, the zinc ion content of the pretreatment composition may be at least 500 ppm, based on total weight of the pretreatment composition, such as at least 800 ppm, and in some instances, may be no more than 1500 ppm, based on total weight of the pretreatment composition, such as no more than 1200 ppm. According to the present invention, the zinc ion content of the aqueous acidic compositions may be 500 ppm to 1500 ppm, based on total weight of the pretreatment composition, such as at least 800 ppm to 1200 ppm. The source of the zinc ion may be conventional zinc ion sources, such as zinc nitrate, zinc oxide, zinc carbonate, zinc metal, and the like.

[0046] According to the present invention, the phosphate content of the pretreatment composition may be at least 8000 ppm, based on total weight of the pretreatment composition, such as at least 12000 ppm, and in some cases may be no more than 20000 ppm, based on total weight of the pretreatment composition, such as no more than 14000 ppm. According to the present invention, the phosphate content of the pretreatment composition may be 8000 ppm to 20000 ppm, based on total weight of the pretreatment composition, such as 12000 ppm to 14000 ppm. The source of phosphate ion may be phosphoric acid, monosodium phosphate, disodium phosphate, and the like.

[0047] The pretreatment composition of the present invention may have a pH of at least 2.5, such as at least 3.0, and in some cases, no more than 5.5, such as no more than 3.5. The pretreatment composition may have a pH of 2.5 to 5.5, such as 3.0 to 3.5.

[0048] According to the present invention, the pretreatment composition may also comprise an accelerator. The accelerator may be present in an amount sufficient to accelerate the formation of the zinc phosphate coating and may be present in the pretreatment composition in an amount of at least 500 ppm, based on total weight of the pretreatment composition, such as at least 1000 ppm, such as at least 2500 ppm, and in some instances may be present in an amount of no more than 20000 ppm, based on total weight of the pretreatment composition, such as no more than 10000 ppm, such as no more than 5000 ppm. According to the present invention, the accelerator may be present in the pretreatment composition in an amount of 500 ppm to 20000 ppm, based on total weight of the pretreatment composition, such as 1000 ppm to 10000 ppm, such as 2500 ppm to 5000 ppm. Useful accelerators may include oximes such as acetaldehyde oxime and acetoxime, nitrites such as sodium nitrite and ammonium nitrite, peroxides such as hydrogen peroxide, or combinations thereof.

[0049] According to the present invention, the pretreatment composition may also comprise fluoride ion, nitrate ion, and various metal ions, such as cobalt ion, calcium ion, magnesium ion, manganese ion, iron ion, copper ion, and the like.

[0050] Fluoride ion may be present in the pretreatment composition in an amount of at least 100 ppm, based on total weight of the pretreatment composition, such as at least 250 ppm, and in some instances may be present in an amount of no more than 2500 ppm, based on total weight of the pretreatment composition, such as no more than 1000 ppm, and in some cases may be present in an amount of 100 ppm to 2500 ppm, based on total weight of the pretreatment composition, such as 250 ppm to 1000 ppm.

[0051] According to the present invention, nitrate ion may be present in the pretreatment composition in an amount of at least 1000 ppm, based on total weight of the pretreatment composition, such as at least 2000 ppm, and in some instances may be present in an amount of no more than 10000 ppm, based on total weight of the pretreatment composition, such as no more than 5000 ppm, and in some cases may be present in an amount of 1000 ppm to 10000 ppm, based on total weight of the pretreatment composition, such as 2000 ppm to 5000 ppm.

[0052] According to the present invention, calcium ion may be present in the pretreatment composition in an amount of at least 100 ppm, based on total weight of the pretreatment composition, such as at least 500 ppm, and in some cases, no more than 4000 ppm, based on total weight of the pretreatment composition, such as no more than 2500 ppm, and in some cases may be present in an amount of 100 ppm to 4000 ppm, based on total weight of the pretreatment composition, such as 500 ppm to 2500 ppm.

[0053] According to the present invention, manganese ion may be present in the pretreatment composition in an amount of at least 100 ppm, based on total weight of the pretreatment composition, such as at least 200 ppm, such as at least 500 ppm, and in some cases no more than 1500 ppm, based on total weight of the pretreatment composition, such as no more than 1000 ppm, such as no more than 800 ppm, and in some cases, in an amount of 100 ppm to 1500 ppm, based on total weight of the pretreatment composition, such as from 200 ppm to 1000 ppm, such as 500 ppm to 800 ppm.

[0054] According to the present invention, iron ion may be present in the pretreatment composition in an amount of at least 5 ppm, based on total weight of the pretreatment composition, such as at least 50 ppm, and in some cases, no more than 500 ppm, based on total weight of the pretreatment composition, such as no more than 300 ppm, and in some cases, may be present in the pretreatment composition in an amount of 5 ppm to 500 ppm, such as 50 ppm to 300 ppm.

[0055] According to the present invention, copper ion may be present in the pretreatment composition in an amount of at least 1 ppm, based on total weight of the pretreatment composition, such as at least 3 ppm, and in some cases, no more than 30 ppm, based on total weight of the pretreatment composition, such as no more than 15 ppm, and in some cases, may be present in the pretreatment composition in an amount of 1 ppm.

[0056] The pretreatment composition of the present invention can be prepared fresh with the above mentioned ingredients in the concentrations specified or can be prepared in the form of aqueous concentrates in which the concentration of the various ingredients is considerably higher such that the concentrates may be diluted with aqueous medium such as water or are diluted by feeding them into a zinc phosphating composition which has been in use for some time. Typical concentrates may contain at least 10,000 ppm zinc ions, based on total weight of the pretreatment composition concentrate, such as at least 12,000 ppm zinc ions, such as at least 16,000 ppm zinc ions, and in some cases may contain no more than 100,000 ppm zinc ions, based on total weight of the pretreatment composition concentrate, such as no more than 30,000 ppm zinc ions, such as no more than 20,000 ppm zinc ions, and in some cases may contain 10,000 ppm to 100,000 ppm zinc ions, based on total weight of the pretreatment composition concentrate, such as 12,000 ppm to 30,000 ppm zinc ions, such as from 16,000 ppm to 20,000 ppm zinc ions.

[0057] The substrate pretreatment system of the present invention may be used in a method of treating a metal substrate comprising contacting at least a portion of a surface of the substrate with the activating rinse comprising a dispersion of metal phosphate particles having a D90 particle size of no greater than 10 µm, wherein the metal phosphate comprises divalent or trivalent metals or combinations thereof, and subsequently contacting at least a portion of the surface that has been contacted with the activating rinse with the pretreatment composition comprising zinc ions and phosphate ions, wherein the pretreatment composition is substantially free of nickel.

[0058] Optionally, the substrate surface to be treated in accordance with the methods of the present invention may be cleaned to remove grease, dirt, or other extraneous matter and/or rinsed prior to applying the activating rinse. Cleaning the substrate surface 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 Chemkleen™ 163, Chemkleen™ 177, Chemkleen™ 181ALP, Chemkleen™ 490MX, and Chemkleen™ 2010LP each of which is commercially available from PPG Industries, Inc.

[0059] Following cleaning, the substrate optionally may be rinsed with tap water, deionized water, and/or an aqueous solution of rinsing agents in order to remove any residue. The wet substrate surface optionally may be dried, such as air dried, for example, by using an air knife or warm air blower.

[0060] According to the present invention, the activating rinse can be applied to the substrate surface by spray, roll-coating or immersion techniques. The activating rinse may be applied onto the substrate at a temperature of, for example, 15°C to 50°C, such as 25°C to 35°C for any suitable period of time, such as at least 1 second, such as at least 10 seconds, such as at least 2 minutes, such as at least 5 minutes.

[0061] According to the present invention, the method for treating a substrate further includes contacting at least a portion of the surface that has been contacted with the activating rinse with the pretreatment composition described above to form a phosphate coating on the surface of the "activated" substrate. The pretreatment composition may be applied by spray application or immersion of the activated substrate in an phosphate bath which contains zinc at a temperature typically ranging from 20°C to 75°C for 1 to 3 minutes. The bath typically may be an acidic phosphate bath and may comprise iron and/or other divalent metals known in the art in addition to the zinc ions, as already discussed above.

[0062] After application of the phosphate coating, the substrate may be optionally post-rinsed with a chromium or non-chromium containing solution, optionally rinsed with water and/or optionally dried. Paint may then be applied, if desired, such as, by electrodeposition or by conventional spray or roll coating techniques.

[0063] The present invention is also directed to a substrate treated with the pretreatment system that is disclosed herein. The substrate may comprise nucleation sites formed from an activating rinse described above, and may further comprise a metal phosphate coating formed from a metal phosphate pretreatment composition described above applied over the nucleation sites formed on at least a portion of the substrate by the activating rinse. The metal phosphate coating may comprise crystals having a crystal size of at least 0.4 μm, such as at least 0.5 μm, such as at least 0.6 μm, such as at least 0.9 μm, and in some cases no larger than 4 μm, such as no larger than 2.7 μm, such as no larger than 2.5 μm, such as no larger than 2 μm. The metal phosphate coating may comprise crystals having a crystal size of 0.4 μm to 4 μm, such as 0.5 μm to 2.5 μm, such as 0.6 μm to 2 μm.

[0064] Crystal size of a phosphate coating may be determined by methods known to those skilled in the art. For example, a representative area of the panel (i.e., a coated area of approximately 1.27 cm by 1.27 cm with no obvious coating defects) may be selected and an image of the representative area may be acquired an image at either 5,000x or 10,000x magnification using a scanning electron microscope (SEM), such as, for example, a Tescan Vega 2 SEM. The magnification utilized will be dependent on the crystal size as high magnification (10,000x) will be required for crystal sizes that are not distinguishable at 5,000x magnification using an SEM. Nine to twelve evenly-spaced crystals, e.g. ten, on each image may be measured using software known to those skilled in the art, such as, for example, ImageJ (version 1.46), and the representative crystal sizes may be averaged to determine crystal size. One skilled in the art will recognize that there can be variations in this procedure that retain the essential elements of microscopic imaging and averaging of representative crystal size.

[0065] In an example, the present invention also may be directed to an activating stage such as those used in an automotive manufacturing facility. According to the present invention, the activating stage comprises immersion of the substrate in a bath which contains the activating rinse of the substrate pretreatment system that is disclosed herein. According to the present invention, the activating rinse is contained within the immersion tank at a temperature of 15°C to 50°C. At least a portion of a surface of the substrate is subjected to the activating rinse by immersing the substrate in the activating rinse for any suitable period of time, e.g. those already described above. After being immersed in the activating rinse, a portion of the activated substrate then may be subjected to a phosphatizing step by applying a metal phosphate pretreatment composition, e.g. a zinc phosphate pretreatment composition, to the activated substrate. It should be noted, however, that prior to the application of the metal phosphate pretreatment composition to the activated substrate, additional activating rinse can be sprayed onto a portion of the activated substrate via a spraying nozzle as the activated substrate is removed from the immersion tank. For example, the spraying nozzle could be a spray bank of nozzles which is positioned downstream from the immersion tank. After the activated substrate exits the immersion tank and/or after additional activating rinse is applied onto the activated substrate, the activated substrate is phosphatized by applying a metal phosphate pretreatment composition to the activated substrate using techniques that are known in the art such as a spray and/or an immersion technique.

[0066] According to the present invention, the activating stage may comprise a number of spraying nozzles that are used to apply the activating rinse bath onto a least a portion of a substrate. Disposed beneath the spraying nozzles is a spray tank which is adapted to collect the activating rinse that exits the spraying nozzles and/or any excess activating rinse that drips off the surface of the activated substrate. The spray tank is connected to the spraying nozzles in a manner that allows the spraying nozzles to utilize the activating rinse that is collected in the spray tank thereby recycling the activating rinse bath. After the activating rinse is applied onto at least a portion of the substrate, the activated substrate is then phosphatized as described in the preceding paragraph.

[0067] According to the present invention, after the substrate is contacted with the pretreatment composition, a coating composition comprising a film-forming resin may be deposited onto at least a portion of the surface of the substrate that has been contacted with the pretreatment composition. Any suitable technique may be used to deposit such a coating composition onto the substrate, including, for example, brushing, dipping, flow coating, spraying and the like. In some instances, however, as described in more detail below, such depositing of a coating composition may comprise an electrocoating step wherein an electrodepositable composition is deposited onto a metal substrate by electrodeposition. In certain other instances, as described in more detail below, such depositing of a coating composition comprises a powder coating step. In still other instances, the coating composition may be a liquid coating composition.

[0068] According to the present invention, the coating composition may comprise a thermosetting film-forming resin or a thermoplastic film-forming resin. 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. 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. 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.

[0069] As previously indicated, according to the present invention, a coating composition comprising a film-forming resin may be deposited onto the substrate 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 ionic, 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.

[0070] According to the present invention, such electrodeposition may be 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.

[0071] According to the present invention, the electrodepositable coating composition may comprise 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).

[0072] According to the present invention, the electrodepositable compositions may contain for instance, 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 may contain cationic functional groups to impart a positive charge.

[0073] Examples of film-forming resins suitable for use in anionic electrodepositable coating 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 interpolymers 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 alkyd-aminoplast vehicle, i.e., a vehicle containing an alkyd resin and an amine-aldehyde resin. Yet another anionic electrodepositable resin composition comprises mixed esters of a resinous polyol, such as is described in United States Patent 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 phosphatized polyepoxide or phosphatized acrylic polymers as are known to those skilled in the art.

[0074] 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 group-containing resins, such as the acid-solubilized reaction products of polyepoxides and primary or secondary amines, such as those described in United States Patent 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 United States Patent No. 3,984,299, or the isocyanate can be partially blocked and reacted with the resin backbone, such as is described in United States Patent No. 3,947,338. Also, one-component compositions as described in United States Patent 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 United States Patent Nos. 3,455,806 and 3,928,157.

[0075] 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 United States Patent Nos. 3,962,165; 3,975,346; and 4,001,101. Examples of other cationic resins are ternary sulfonium salt group-containing resins and quaternary phosphonium salt-group containing resins, such as those described in United States Patent 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 United States Patent No. 4,134,932, can be used.

[0076] According to the present invention, the resins present in the electrodepositable composition are positively charged resins which contain primary and/or secondary amine groups, such as described in United States Patent Nos. 3,663,389; 3,947,339; and 4,116,900. In United States Patent No. 3,947,339, a polyketimine derivative of a polyamine, such as diethylenetriamine or triethylenetetraamine, 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 diethylenetriamine and triethylenetetraamine, and the excess polyamine vacuum stripped from the reaction mixture, as described in United States Patent Nos. 3,663,389 and 4,116,900.

[0077] According to the present invention, the active hydrogen-containing ionic electrodepositable resin may be 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 electrodeposition bath.

[0078] 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.

[0079] Aminoplast resins may be used as the curing agent for anionic electrodeposition, are the condensation products of amines or amides with aldehydes. Examples of suitable amines 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 methylol groups or similar alkylol groups depending on the particular aldehyde employed. Often, these methylol 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.

[0080] 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 United States Patent 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 United States Patent 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.

[0081] Suitable polyisocyanates include aromatic and aliphatic polyisocyanates, including cycloaliphatic polyisocyanates and representative examples include diphenylmethane-4,4'-diisocyanate (MDI), 2,4- or 2,6-toluene diisocyanate (TDI), including mixtures thereof, p-phenylene diisocyanate, tetramethylene and hexamethylene diisocyanates, dicyclohexylmethane-4,4'-diisocyanate, isophorone diisocyanate, mixtures of phenylmethane-4,4'-diisocyanate and polymethylene polyphenylisocyanate. Higher polyisocyanates, such as triisocyanates can be used. An example would include triphenylmethane-4,4',4"-triisocyanate. Isocyanate prepolymers with polyols such as neopentyl glycol and trimethylolpropane and with polymeric polyols such as polycaprolactone diols and triols (NCO/OH equivalent ratio greater than 1) can also be used.

[0082] The polyisocyanate curing agents are typically utilized in conjunction with the active hydrogen containing cationic 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.

[0083] The electrodepositable coating compositions described herein may in particular be in the form of an aqueous dispersion. The average particle size of the resinous phase is generally less than 1.0 micron and usually less than 0.5 microns, often less than 0.15 micron.

[0084] 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 coating compositions are in the form of resin concentrates, they generally have a resin solids content of 20 to 60 percent by weight based on weight of the aqueous dispersion.

[0085] The electrodepositable coating 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.

[0086] As aforementioned, besides water, the aqueous medium may contain a coalescing solvent. Useful coalescing solvents are often hydrocarbons, alcohols, esters, ethers and ketones. Coalescing solvents that may be used may be alcohols, polyols and ketones. Specific coalescing solvents include isopropanol, butanol, 2-ethylhexanol, isophorone, 2-methoxypentanone, ethylene and propylene glycol and the monoethyl monobutyl and monohexyl 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.

[0087] After deposition of the electrodepositable coating composition, 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. According to the invention, the thickness of the resultant film is from 10 to 50 microns.

[0088] Alternatively, as mentioned above, according to the present invention, after the substrate has been contacted with the pretreatment composition, a powder coating composition may then be deposited onto at least a portion of the surface of the substrate that has been contacted with the pretreatment composition. As used herein, “powder coating composition” refers to a coating composition which is completely free of water and/or solvent. Accordingly, the powder coating composition disclosed herein is not synonymous to waterborne and/or solvent-borne coating compositions known in the art.

[0089] According to the present invention, the powder coating composition comprises (a) a film forming polymer having a reactive functional group; and (b) a curing agent that is reactive with the functional group. Examples of powder coating compositions that may be used in the present invention include the polyester-based ENVIROCRON line of powder coating compositions (commercially available from PPG Industries, Inc.) or epoxy-polyester hybrid powder coating compositions. Alternative examples of powder coating compositions that may be used in the present invention include low temperature cure thermosetting powder coating compositions comprising (a) at least one tertiary aminourea compound, at least one tertiary aminourethane compound, or mixtures thereof, and (b) at least one film-forming epoxy-containing resin and/or at least one siloxane-containing resin (such as those described in US Patent No. 7,470,752, assigned to PPG Industries, Inc. and incorporated herein by reference); curable powder coating compositions generally comprising (a) at least one tertiary aminourea compound, at least one tertiary aminourethane compound, or mixtures thereof, and (b) at least one film-forming epoxy-containing resin and/or at least one siloxane-containing resin (such as those described in US Patent No. 7,432,333, assigned to PPG Industries, Inc. and incorporated herein by reference); and those ccomprising a solid particulate mixture of a reactive group-containing polymer having a T_g of at least 30°C (such as those described in US Patent No. 6,797,387, assigned to PPG Industries, Inc. and incorporated herein by reference).

[0090] Suitable film forming polymers that may be used in the powder coating composition of the present invention comprise a (poly)ester (e.g., polyester triglycidyl isocyanurate), a (poly)urethane, an isocyanurate, a (poly)urea, a (poly)epoxy, an anhydride, an acrylic, a (poly)ether, a (poly)sulfide, a (poly)amine, a (poly)amide, (poly)vinyl chloride, (poly)olefin, (poly)vinylidene fluoride, or combinations thereof.

[0091] According to the present invention, the reactive functional group of the film forming polymer of the powder coating composition comprises hydroxyl, carboxyl, isocyanate (including blocked (poly)isocyanate), primary amine, secondary amine, amide, carbamate, urea, urethane, vinyl, unsaturated ester, maleimide, fumarate, anhydride, hydroxyl alkylamide, epoxy, or combinations thereof.

[0092] Suitable curing agents (crosslinking agents) that may be used in the powder coating composition of present invention comprise an aminoplast resin, a polyisocyanate, a blocked polyisocyanate, a polyepoxide, a polyacid, a polyol, or combinations thereof.

[0093] After deposition of the powder coating composition, 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 150°C to 200°C, such as from 170°C to 190°C, for a period of time ranging from 10 to 20 minutes. According to the invention, the thickness of the resultant film is from 50 microns to 125 microns.

[0094] As mentioned above, the coating composition may be a liquid coating composition. As used herein, “liquid coating composition” refers to a coating composition which contains a portion of water and/or solvent. Accordingly, the liquid coating composition disclosed herein is synonymous to waterborne and/or solventborne coating compositions known in the art.

[0095] As mentioned above, according to the present invention, the coating composition may be a liquid coating composition. As used herein, "liquid coating composition" refers to a coating composition which contains a portion of water and/or solvent. Accordingly, the liquid coating composition disclosed herein is synonymous to waterborne and/or solventborne coating compositions known in the art.

[0096] According to the present invention, the liquid coating composition may comprise, for example, (a) a film forming polymer having a reactive functional group; and (b) a curing agent that is reactive with the functional group. In other examples, the liquid coating may contain a film forming polymer that may react with oxygen in the air or coalesce into a film with the evaporation of water and/or solvents. These film forming mechanisms may require or be accelerated by the application of heat or some type of radiation such as Ultraviolet or Infrared. Examples of liquid coating compositions that may be used in the present invention include the SPECTRACRON® line of solventbased coating compositions, the AQUACRON® line of waterbased coating compositions, and the RAYCRON® line of UV cured coatings (all commercially available from PPG Industries, Inc.).

[0097] Suitable film forming polymers that may be used in the liquid coating composition of the present invention may comprise a (poly)ester, an alkyd, a (poly)urethane, an isocyanurate, a (poly)urea, a (poly)epoxy, an anhydride, an acrylic, a (poly)ether, a (poly)sulfide, a (poly)amine, a (poly)amide, (poly)vinyl chloride, (poly)olefin, (poly)vinylidene fluoride, (poly)siloxane, or combinations thereof.

[0098] According to the present invention, the reactive functional group of the film forming polymer of the liquid coating composition may comprise hydroxyl, carboxyl, isocyanate (including blocked (poly)isocyanate), primary amine, secondary amine, amide, carbamate, urea, urethane, vinyl, unsaturated ester, maleimide, fumarate, anhydride, hydroxyl alkylamide, epoxy, or combinations thereof.

[0099] Suitable curing agents (crosslinking agents) that may be used in the liquid coating composition of the present invention may comprise an aminoplast resin, a polyisocyanate, a blocked polyisocyanate, a polyepoxide, a polyacid, a polyol, or combinations thereof.

[00100] In addition, a colorant and, if desired, various additives such as surfactants, wetting agents or catalyst can be included in the coating composition (electrodepositable, powder, or liquid). 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.

[00101] 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 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.

[00102] 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.

[00103] 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.

[00104] 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.

[00105] 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 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 re-agglomeration of nanoparticles within the coating, a dispersion of resin-coated nanoparticles can be used. As used herein, a "dispersion of resin-coated nanoparticles" refers to a continuous phase in which is dispersed discreet "composite microparticles" that comprise a nanoparticle and a resin coating on the nanoparticle. Example dispersions of resin-coated nanoparticles and methods for making them are identified in United States Patent Application Publication 2005-0287348 A1, 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.

[00106] 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. According to the invention, 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.

[00107] According to the invention, 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. According to the invention, 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.

[00108] According to the invention, 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 according to the 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, incorporated herein by reference.

[00109] 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.

[00110] According to the present invention, it has been unexpectedly and surprisingly discovered that the application of the activating rinse disclosed herein to a surface of the metal substrate prior to application of the metal phosphate pretreatment composition enables the bath containing the metal phosphate pretreatment composition to be maintained (and therefore the metal phosphate pretreatment composition to be applied) at a lower temperature than methods employing conventional activating rinses, such as Jernstedt type activators or other zinc phosphate activating rinses comprising metal phosphate particles having a D_{90} particle size of greater than 10 μm. As G. W. Jernstedt discovered the beneficial effects of activating metal surfaces by treating them with a solution containing titanium together with sodium phosphate prior to zinc phosphating, titanium containing activating compositions are now generally referred to as "Jernstedt type activators". For example, according to the present invention, the phosphate bath containing the nickel-free metal phosphate pretreatment composition may be at a temperature of no greater than 60°C, such as no greater than 50°C, such as no greater than 40°C, such as no greater than 30°C, such as no greater than 25°C. According to the present invention, the temperature of the bath containing the nickel-free metal phosphate pretreatment composition may range from 20°C to 60°C, such as from 25°C to 50°C, such as from 30°C to 40°C. According to the present invention, application of the activating rinse disclosed herein to a surface of the metal substrate prior to application of the nickel-free metal phosphate pretreatment composition may enable the bath containing the nickel-free metal phosphate pretreatment composition to be maintained at room temperature (20°C).

[00111] It also has been unexpectedly and surprisingly discovered that application of the activating rinse disclosed herein to a surface of the metal substrate prior to application of the nickel-free metal phosphate pretreatment composition results in a metal phosphate coating formed on the substrate surface that has a lower coating weight, smaller phosphate crystal size, increased coating coverage, and improved adhesion performance compared to metal phosphate coatings formed on substrate surfaces treated with conventional activating rinses, such as Jernstedt type activators or activating rinses comprising metal phosphate particles having a D_{90} particle size of greater than 10 µm. While not wishing to be bound by theory, it is believed that smaller phosphate crystal sizes are the result of faster reaction of the activating rinse with the substrate surface and impart more complete coverage of the substrate surface with nucleation sites, which leads to more complete coverage of the substrate surface with the subsequently applied nickel-free metal phosphate-containing pretreatment composition.

[00112] As used herein, unless indicated otherwise, a plural term can encompass its singular counterpart and vice versa, unless indicated otherwise. For example, although reference is made herein to “a” metal sulfate salt and “a” dispersant, a combination (i.e., a plurality) of these components can be used. 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.

[00113] As used herein, “including,” “containing” and like terms are understood in the context of this application to be synonymous with “comprising” and are therefore open-ended and do not exclude the presence of additional undescribed or unrecited elements, materials, ingredients or method steps. As used herein, “consisting of” is understood in the context of this application to exclude the presence of any unspecified element, ingredient or method step. As used herein, “consisting essentially of” is understood in the context of this application to include the specified elements, materials, ingredients, solvents, or method steps, where applicable, while other non-specified materials are not purposefully added to the composition and are only present as impurities in a combined amount of less than 5% by weight based on a total weight of the composition.

[00114] As used herein, unless indicated otherwise, the term “substantially free” means that a particular material is not purposefully added to the activating rinse, and is only present as an impurity in a trace amount of less than 1% by weight based on a total weight of the activating rinse. As used herein, unless indicated otherwise, the term “completely free” means that an activating rinse does not comprise a particular material, i.e., the activating rinse comprises 0% by weight of such material.

[00115] 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 such as those expressing values, amounts, percentages, ranges, subranges and fractions may be read as if prefaced by the word “about,” even if the term does not expressly appear. 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. Notwithstanding that the numerical ranges and parameters setting forth 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. 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. Where a closed or open-ended numerical range is described herein, all numbers, values, amounts, percentages, subranges and fractions within or encompassed by the numerical range are to be considered as being specifically included in and belonging to the original disclosure of this application as if these numbers, values, amounts, percentages, subranges and fractions had been explicitly written out in their entirety.

[00116] Illustrating the invention are the following examples that are not to be considered as limiting the invention to their details. All parts and percentages in the examples, as well as throughout the specification, are by weight unless otherwise indicated.

EXAMPLES

Activating Rinse Compositions

[00117] The following activating rinse compositions were prepared as follows:

[00118] RC: RC (a Jernstedt-type activating rinse concentrate commercially available from PPG Industries, Inc., also known as VERSABOND® RC) was diluted in deionized (DI) water to a concentration of 1 g concentrate/L DI water to prepare a bath containing the activating rinse composition.

[00119] RC30: 1.1 grams of RC30 (a zinc phosphate-based activating rinse concentrate with an average zinc phosphate particle size of about 1 μm and a D_{90} of 1-3 μm, commercially available from PPG Industries, Inc., also known as VERSABOND® 30) was added to 1 liter of deionized water to produce a dispersion of zinc phosphate with a concentration of 1.1 g/L.

[00120] Micromedia-milled zinc phosphate-based activator (MMM): Micromedia-milled zinc phosphate (MMM) is a zinc phosphate-based activating rinse that was prepared as follows: 1288.4 grams of zinc phosphate pigment was sifted into a pre-blended mixture of 724 grams deionized water, 787.7 grams of dispersant (Disperbyk-190, commercially available from BYK-Chemie GmbH), and 25.6 grams of defoamer (BYK-011, commercially available from BYK-Chemie GmbH) and mixed for 30 minutes using a Fawcett Air Mixer, model LS-103A with a type 1 angled tooth/Cowles style blade. This mixture was then milled in recirculation mode through an Eiger Mini 250 horizontal media mill (from EMImills) containing 1.2-1.7 mm zirconium oxide media for 8.1 minutes of residence time. To 1695.7 grams of this preliminary dispersion was added 150.3 grams of deionized water. This material was then milled in recirculation mode through the above-described Eiger mill, except that 0.3 mm zirconium oxide media was used. The mixture was milled for an additional 40.1 minutes residence time. An additional 718 grams of deionized water, as well as 158.3 grams Disperbyk-190 and 2 grams of Byk-011, were added throughout the milling process. Several interim process samples were taken throughout the milling, such that a final yield of 1657.3 grams was obtained. This material had a concentration of 27% by weight of zinc phosphate. 1.85 grams of the above dispersion of zinc phosphate was mixed per liter of deionized water, to give an activator bath with a zinc phosphate concentration of 0.5 grams per liter.

[00121] In the Examples that follow, some activating baths included metal sulfates of the type and in the amounts indicated in Tables 1 and 2, below.

Nickel-Free Phosphate Pretreatment Composition

[00122] A nickel-free zinc phosphate pretreatment concentrate was prepared by carefully combining the following materials and mixing thoroughly until clear:

Chemical	**Quantity**
Phosphoric Acid (85%), available from Fisher Chemical	595.6 grams
Nitric Acid (Reagent Grade), available from Fisher Chemical	28.7 grams
Zinc Oxide, available from Umicore Zinc Chemicals	62.25 grams
Manganese Oxide, available from Sigma-Aldrich Corporation	32.7 grams
Acetaldoxime (50% wt), available from Sigma-Aldrich Corporation	1.95 grams
Ferrous Sulfate, available from Sigma-Aldrich Corporation	3.75 grams
Dowfax 2A1 Surfactant, available from The Dow Chemical Co.	1.05 grams
50% Sodium Hydroxide Solution, available from The Dow Chemical Co.	72 grams
Deionized Water	702 grams

[00123] Five gallons of a nickel-free zinc phosphate pretreatment bath was then prepared by adding the following materials in order into deionized water:

Chemical	**Quantity**
Nickel-free zinc phosphate concentrate	756 grams
Chemfos® 700 F* (partially neutralized fluosilicic acid)	56.75 grams
Chemfos® 700 F/F* (a solution of ammonium bifluoride)	122.85 grams
Chemfos® AZN* (zinc nitrate solution)	15.4 grams
Acetaldoxime (50% w/w)	8.505 grams
Hydrogen Peroxide (30% w/w), available from Acros Organics	1.7 grams
Buffer M* (a solution of strong base)	321.3 grams

*Materials available from PPG Industries, Inc.

[00124] The nickel-free zinc phosphate pretreatment bath was adjusted to a free acid value of 0.8-1.0 mL with Buffer M. The free acid value was measured by titrating a 10 mL sample of the bath with 0.1 N sodium hydroxide solution, using bromophenol blue as an indicator and titrating to a blue-gray endpoint.

Example 1

[00125] Four hot dipped galvanized panels (4 inches x 6 inches, automotive-grade material from Salzgitter Mannesmann Stahlservice GmbH) and four cold rolled steel panels (4.13 inches x 6 inches, standard test panels from Chemetall GmbH) were spray cleaned with a mixture of Chemkleen 2010LP (1.25% v/v)/Chemkleen 181ALP (0.125% v/v) for 2 minutes at 49°C followed by immersion rinse in DI water for 15 seconds and spray rinse with DI water for 15 seconds. Panels were then immersed in a bath (20°C-25°C) containing the MMM activating rinse (either with or without metal sulfate, pre-dissolved in a minimal amount of DI water before being added to the MMM activating rinse, as shown in Table 1) for 1 minute. All panels were then immersed in the nickel-free zinc phosphate pretreatment bath (50°C) for 3 minutes. Panels then were spray rinsed with DI water for 20-30 seconds. Panels were warm air dried using a Hi-Velocity handheld blow-dryer made by Oster® (model number 078302-300-000) on high-setting at a temperature of about 50-55°C until the panel was dry (about 1-5 minutes).

[00126] For each run, one panel was used to determine phosphate coating completeness. The other panel was cut in half to yield two panels each 2"x 3" and one of the half panels was used to determine coating weight and the other half panel was used to determine average crystal size.

[00127] Zinc phosphate coating weight was determined on one of the 2"x 3" panels by the weigh-strip-weigh method. Treated panels were weighed on an analytical balance to the nearest 0.1 mg. Cold roll steel panels were immersed in a solution comprised of 100 g sodium hydroxide pellets and 25 milliliters 98% triethanolamine diluted to 1 liter total volume with deionized water for 1.5 minutes to dissolve all of the zinc phosphate coating off of the panels without dissolution of the substrate. Hot dipped galvanized steel panels were immersed in a solution comprised of 16 g ammonium dichromate [$(NH_4)_2Cr_2O_7$] dissolved into 1 liter concentrated ammonium hydroxide for 2 minutes to dissolve all of the zinc phosphate coating off of the panels without dissolution of the substrate. After the stripping procedure, panels were rinsed thoroughly with deionized water, wiped gently with a tissue to remove any loosely-adherent phosphate coating, rinsed with deionized water again, and dried in warm air by using a Hi-Velocity handheld blow-dryer made by Oster® (model number 078302-300-000) on high-setting at a temperature of about 50-55°C until the panel was dry, typically 1-5 minutes. The dried panel was then weighed, and the weight loss was used to calculate the coating weight per unit area.

[00128] Zinc phosphate average crystal size was determined on 2"x 3" panels by first selecting a representative area of the panel, i.e., a coated area of approximately 0.5 inch by 0.5 inch near the center of the 2"x3" panel with no obvious coating defects, then acquiring an image at either 5,000x or 10,000x magnification using a Tescan Vega 2 scanning electron microscope (SEM). The magnification was determined by the crystal size with the 10,000x magnification required for smaller crystal sizes. Nine to twelve evenly-spaced crystals on each image were measured using ImageJ software (version 1.46), and the results averaged.

ImageJ software is public domain software, available from http://imagej.nih.gov/ij/. Further details of the method have already been described above.

[00129] Following pretreatment, for each run, two panels of the treated panels then were electrocoated using Enviroprime NT, a cathodic electrocoat available from PPG Industries, Inc. and applied according to the manufacturer's instructions. The electrodeposition was carried out at 220 volts, using a 30 second ramp. The electrodeposition bath temperature was 90°F. The current density was 1.5 A/ft^2 and the panels were coated to 27 Coulombs to reach a dry film thickness of 18-20 µm.

[00130] The electrocoated panels were tested for paint adhesion (dry adhesion and exposed adhesion, described in more detail below) by crosshatching and tape-pulling. For the dry adhesion test, a razor blade was used to scribe eleven lines parallel and perpendicular to the length of the one of the electrocoated panels. The resultant grid area of the scribed lines was 0.5" x 0.5" to 0.75" to 0.75" square. Dry adhesion was assessed by using 3M's Scotch 610 tape, which was firmly adhered over the scribed grid area by finger rubbing it multiple times prior to pulling it off. The crosshatch area was evaluated for paint loss on a scale from 0 to 10, with 0 being total paint loss and 10 being absolutely no paint loss. An adhesion value of 7 is considered acceptable in the automotive industry. For the exposed adhesion test, following electrodeposition, the other panel was immersed in deionized water (40°C) for ten days, at which time the panels were removed, wiped with a towel to dry and allowed to sit at ambient temperature for one hour prior to crosshatching and tape-pulling to evaluate paint adhesion as described above.

[00131] Metal phosphate coating weight (g/m^2), metal phosphate crystal size, and dry and exposed adhesion performance for the treated panels are reported in Table 1, below.

Table 1

Activating Rinse	**Metal Sulfate**	**Hot Dipped Galvanized**			
		Coating Weight (g/m^2)	**Crystal Size (µm)**	**Dry Adhesion**	**Exposed Adhesion**
MMM (Comparative)	None	4.0	1.8	10	0
MMM	Zinc Sulfate (66 ppm zinc, 100 ppm sulfate)	3.7	1.8	9	0
MMM	Nickel Sulfate (61 ppm nickel, 100 ppm sulfate)	2.1	1.0	9	9
MMM	Cobalt Sulfate (62 ppm cobalt, 100 ppm sulfate)	2.1	0.9	9	9
	Metal Sulfate	**Cold Rolled Steel**			

Activating Rinse		**Coating Weight (g/m²)**	**Crystal Size (µm)**	**Dry Adhesion**	**Exposed Adhesion**
MMM (Comparative)	None	0.9	3.1	10	10
MMM	Zinc Sulfate (66 ppm zinc, 100 ppm sulfate)	0.8	2.2	10	10
MMM	Nickel Sulfate (61 ppm nickel, 100 ppm sulfate)	0.8	2.4	10	10
MMM	Cobalt Sulfate (62 ppm cobalt, 100 ppm sulfate)	-	2.3	10	10

[00132] As shown in Table 1, immersion of hot dipped galvanized steel panels in activating baths made from MMM activating rinse compositions that did not include a metal sulfate or that included zinc sulfate had an exposed adhesion value of zero, indicating extremely poor adhesion. In contrast, when panels were immersed in activating baths made from activating rinse compositions that included either nickel sulfate or cobalt sulfate, exposed adhesion performance was significantly improved to a rating of 9. As stated above, an adhesion value of at least 7 is considered acceptable in the automotive industry. Inclusion of nickel sulfate or cobalt sulfate in the activating rinse composition also resulted in a decreased coating weight and decreased crystal size.

Example 2

[00133] For each run shown in Table 2, four "North American" hot dipped galvanized (HDG) panels (4 inches x 6 inches, from ACT Test Panels) and four "European" HDG panels (4.13 inches x 6 inches, from Chemetall GmbH) were spray cleaned with a mixture of Chemkleen 2010LP (1.25% v/v)/Chemkleen 181ALP (0.125% v/v) for 2 minutes at 49°C followed by immersion rinse in DI water for 15 seconds and spray rinse with DI water for 15 seconds. Panels were then immersed in a bath (20°C-25°C) containing either the RC, RC30, or MMM activating rinse (either with or without metal sulfate, as shown in Table 1) for 1 minute. Panels were then immersed in either a nickel-free zinc phosphate pretreatment bath (30°C or 50°C) for 3 minutes or a nickel-containing zinc phosphate pretreatment bath (50°C) for 3 minutes. Panels then were spray rinsed with DI water for 20-30 seconds. Panels were warm air dried using a Hi-Velocity handheld blow-dryer made by Oster® (model number 078302-300-000) on high-setting at a temperature of about 50-55°C until the panel was dry (about 1-5 minutes).

[00134] Coating weight and average zinc phosphate crystal size was measured as described in Example 1.

[00135] Two panels were electrocoated using Enviroprime NT, a cathodic electrocoat available from PPG Industries, Inc. using the same process described in Example 1. One panel was then tested by the dry adhesion test and the other panel was tested by the exposed adhesion test, as described in Example 1.

[00136] Coating weight (g/m^2), crystal size, and dry and exposed adhesion performance for the treated North American HDG panels are reported in Table 2 and for the treated European HDG panels are reported in Table 3.

Table 2

Activating Rinse	Metal Sulfate	Zinc Phosphate-containing Pretreatment Bath Temp.	North American HDG			
			Coating Weight (g/m^2)	Crystal Size (µm)	Dry Adhesion	Exposed Adhesion
Treatment with Comparative Nickel-containing Phosphate Pretreatment Composition						
RC	None	50°C	2.7	2.0	10	10
RC30	None	50°C	3.3	2.0	10	10
Treatment with Nickel-free Phosphate Pretreatment Composition						
RC	None	50°C	3.0	2.6	10	0
RC	Nickel Sulfate (61 ppm nickel, 100 ppm sulfate)	50°C	3.1	4.6	10	2
RC30	None	50°C	4.6	3.4	10	7
RC30	Nickel Sulfate (61 ppm nickel, 100 ppm sulfate)	50°C	3.9	2.7	10	9
MMM	None	50°C	4.1	2.4	10	6
MMM	Nickel Sulfate (31 ppm nickel, 50 ppm sulfate)	50°C	4.2	1.9	10	7
MMM	Nickel Sulfate (61 ppm nickel, 100 ppm sulfate)	50°C	3.3	1.0	9	8
MMM	Nickel Sulfate (122 ppm nickel, 200 ppm sulfate)	50°C	2.3	1.0	10	10
MMM	Nickel Sulfate (305 ppm nickel, 500 ppm sulfate)	50°C	1.8	1.0	10	10
MMM	Nickel Sulfamate (61 ppm nickel, 200 ppm sulfamate)	50°C	3.9	1.7	9	0

MMM	Nickel Nitrate (61 ppm nickel, 129 ppm nitrate)	50°C	4.5	1.3	10	0
MMM	Nickel Chloride (61 ppm nickel, 74 ppm chloride)	50°C	4.0	1.6	9	3
MMM	Nickel Acetate (61 ppm nickel, 123 ppm acetate)	50°C	4.2	2.1	8	2
MMM	Cobalt Sulfate (31 ppm cobalt, 50 ppm sulfate)	50°C	3.3	1.5	9	7
MMM	Cobalt Sulfate (62 ppm cobalt, 100 ppm sulfate)	50°C	3.0	1.8	10	8
MMM	Cobalt Sulfate (124 ppm cobalt, 200 ppm sulfate)	50°C	1.8	1.0	9	9
MMM	Cobalt Sulfate (310 ppm cobalt, 500 ppm sulfate)	50°C	1.6	0.8	10	10
MMM	None	30°C	6.0	4.2	10	0
MMM	Nickel Sulfate (31 ppm nickel, 50 ppm sulfate)	30°C	4.4	0.6	10	7
MMM	Cobalt Sulfate (62 ppm cobalt, 100 ppm sulfate)	30°C	3.1	0.6	9	7

Table 3

Activating Rinse	**Metal Sulfate**	**European HDG**				
		Zinc Phosphate-containing Pretreatment Bath Temp.	**Coating Weight (g/m²)**	**Crystal Size (µm)**	**Dry Adhesion**	**Exposed Adhesion**
Treatment with Comparative Nickel-containing Phosphate Pretreatment Composition						
RC (Jernstedt)	None	50°C	2.9	2.1	10	10
RC30	None	50°C	3.2	1.8	10	10
Treatment with Nickel-Free Phosphate Pretreatment Composition						
RC (Jernstedt)	None	50°C	2.9	3.5	10	0
RC (Jernstedt)	Nickel Sulfate (61 ppm nickel, 100 ppm sulfate)	50°C	3.2	4.2	10	0
RC30	None	50°C	5.2	3.9	10	7
RC30	Nickel Sulfate (61 ppm nickel, 100 ppm sulfate)	50°C	3.5	2.0	9	8
MMM	None	50°C	4.6	2.1	9	7
MMM	Nickel Sulfate (31 ppm nickel, 50 ppm sulfate)	50°C	4.0	1.8	9	6

MMM	Nickel Sulfate (61 ppm nickel, 100 ppm sulfate)	50°C	3.1	0.7	8	7
MMM	Nickel Sulfate (122 ppm nickel, 200 ppm sulfate)	50°C	2.4	0.9	10	10
MMM	Nickel Sulfate (305 ppm nickel, 500 ppm sulfate)	50°C	1.6	1.1	10	10
MMM	Nickel Sulfamate (61 ppm nickel, 200 ppm sulfamate)	50°C	3.4	1.0	8	1
MMM	Nickel Nitrate (61 ppm nickel, 129 ppm nitrate)	50°C	4.0	0.9	9	1
MMM	Nickel Chloride (61 ppm nickel, 74 ppm chloride)	50°C	3.8	1.5	10	1
MMM	Nickel Acetate (61 ppm nickel, 123 ppm acetate)	50°C	3.7	0.9	9	0
MMM	Cobalt Sulfate (31 ppm cobalt, 50 ppm sulfate)	50°C	2.7	1.2	7	7
MMM	Cobalt Sulfate (62 ppm cobalt, 100 ppm sulfate)	50°C	2.8	1.3	9	8
MMM	Cobalt Sulfate (124 ppm cobalt, 200 ppm sulfate)	50°C	1.7	0.7	10	10
MMM	Cobalt Sulfate (310 ppm cobalt, 500 ppm sulfate)	50°C	1.7	0.7	10	10
MMM	None	30°C	6.0	3.1	10	0
MMM	Nickel Sulfate (31 ppm nickel, 50 ppm sulfate)	30°C	4.1	0.7	10	1
MMM	Cobalt Sulfate (62 ppm cobalt, 100 ppm sulfate)	30°C	3.8	0.5	10	9

[00137] The results in Tables 2 and 3 show that the inclusion of nickel sulfate or cobalt sulfate in RC30 or MMM activating rinse results in reduced crystal size and coating weight of a subsequently applied nickel-free zinc phosphate coating compared to the use of activating rinses that do not include nickel sulfate or cobalt sulfate. Table 2 further shows that the inclusion of nickel sulfate or cobalt sulfate in an activating rinse generally improves the dry and exposed adhesion of a subsequently applied electrodepositable coating over the phosphate coating, even when the zinc phosphate pretreatment composition was applied at low-temperatures.

Example 3

[00138] Comparative Example I was made according to Example 2 of US Publication 2012/0160129A1 to Inbe. RC and Composition 2A were made as described above.

[00139] The dispersion of Comparative I was characterized as follows and was compared to the activation properties of Composition 2A.

[00140] X-ray diffraction of dried solids of Comparative I showed both ZnO and zinc phosphate.

[00141] Particle size (D_{10}, D_{50}, and D_{90}) were measured using a Mastersizer 2000 (available from Malvern Instruments, Ltd., of Malvern, Worcestershire, UK). A laser beam (0.633 mm diameter, 633 nm wavelength) was directed through a dispersion of particles (in deionized water to 2-3% obscuration). The light scattering of the dispersion was measured (measurement parameters 25°C, 2200 RPM, 30 sec premeasurement delay, 10 sec background measurement, 10 sec sample measurement) and the data were analyzed by computer software (Malvern Mastersizer 2000 software, version 5.60) to generate a particle size distribution, from which particle sizes (mean, D_{10}, D_{50}, and D_{90}) were determined and are reported in Table 4.

Table 4.

Sample	Mean PS (μ)	D10 (μ)	D50 (μ)	D90 (μ)
Composition I (Initial)	3.914	1.528	3.495	6.904
Composition I (60 min)	0.643	0.125	0.456	1.31
Composition I (120 min)	0.493	0.109	0.338	0.985
Composition I (180 min)	0.474	0.096	0.284	0.917
Composition 2A	0.181	0.068	0.119	0.332
Composition RC30	0.846	0.079	0.215	2.75

[00142] For each run shown in Table 5, cold rolled steel, electrogalvanized steel, or aluminum alloy 6022 panels (4”x6”, all available from ACT Test Panels, LLC) were spray cleaned with a mixture of Chemkleen 2010LP (1.25% v/v)/Chemkleen 181ALP (0.125% v/v) for 2 minutes at 49°C/120F followed by immersion rinse in DI water for 15 seconds and spray rinse with DI water for 15 seconds. Panels were then immersed in a bath (20°C-25°C) containing either Comparative Example I or Composition 2A, as shown in Table 5, for 1 minute. Activated panels (Comparative Example I or Composition 2A) then were immersed in a zinc phosphate pretreatment bath (made from Chemfos 700AL, commercially available from PPG Industries, Inc., prepared according to instructions provided by the supplier) at a bath temperature of either 78F for 2 minutes. All panels then were spray rinsed with DI water for 20-30 seconds. Panels were warm air dried using a Hi-Velocity handheld blow-dryer made by Oster® (model number 078302-300-000) on high-setting at a temperature of about 50-55°C until the panel was dry (about 1-5 minutes).

[00143] For each run, one of the panels was used to determine phosphate coating completeness. The other panel was cut in half to yield two panels each 2"x 3" and one of the half panels was used to determine coating weight and the other half panel was used to determine average crystal size.

[00144] Zinc phosphate coating completeness and coating weight were determined as described in Example 1. Zinc phosphate average crystal size was determined as described in Example 1. Data are reported in Table 5, below.

Table 5.

Substrate	Activator	Coating Completeness	Crystal size (μm)	Coating weight (mg/ft²)
Cold rolled steel	Composition 2A	100%	1.20	94
Cold rolled steel	Comparative I	60%	2.88	153
Electrogalvanized steel	Composition 2A	100%	1.22	289
Electrogalvanized steel	Comparative I	100%	3.00	359
Aluminum alloy 6022	Composition 2A	95%	1.45	142
Aluminum alloy 6022	Comparative I	40%	3.05	153

[00145] As shown in Table 5, Composition 2A gave 100% coating completeness on CRS and 95% coating completeness on aluminum alloy 6022 panels. In contrast, Comparative I gave only 60% coating completeness on CRS and 40% coating completeness on aluminum alloy 6022 panels. Both Composition 2A and Comparative I gave 100% coating completeness on EG steel panels, but the skilled artisan understands that EG panels are typically 100% coated. Also as shown in Table 5, additionally, crystal size was smaller and coating weight was lower on panels treated with Composition 2A than those treated with Comparative I, regardless of substrate.

[00146] It will be appreciated by skilled artisans that numerous modifications and variations are possible in light of the above disclosure without departing from the broad inventive concepts described and exemplified herein. Accordingly, it is therefore to be understood that the foregoing disclosure is merely illustrative of various exemplary aspects of this application and that numerous modifications and variations can be readily made by skilled artisans which are within the spirit and scope of this application and the accompanying claims.

ASPECTS OF THE INVENTION

1. A substrate pretreatment system, comprising:

a) an activating rinse for treating at least a portion of a substrate comprising a dispersion of metal phosphate particles having a D_{90} particle size of no greater than 10 μm, wherein the metal phosphate comprises divalent or trivalent metals or combinations thereof; and

b) a pretreatment composition for treating at least a portion of the substrate treated with the activating rinse, comprising zinc ions and phosphate ions, wherein the pretreatment composition is substantially free of nickel.

2. The pretreatment system of Aspect 1, wherein the D_{90} particle size is measured from a sample of the activating rinse that has been sonicated.

3. The pretreatment system of Aspect 1 or 2, wherein the activating rinse further comprises a metal sulfate salt, wherein the sulfate of the metal sulfate salt is present in an amount of 5 ppm to 5000 ppm based on a total weight of the activating rinse.

4. The pretreatment system of any of the preceding Aspects, wherein the metal phosphate particles have a D_{90} particle size of no more than 1 μm, preferably of 50 nm to 500 nm.

5. The pretreatment system of any of the preceding Aspects, wherein the divalent or trivalent metals of the metal phosphate in the activating rinse comprise zinc, iron or a combination thereof.

6. The pretreatment system of any of the preceding Aspects, wherein the activating rinse comprises a dispersant comprising non-ionic polymers.

7. The pretreatment system of any of the preceding Aspects, wherein the activating rinse is substantially free of ionic dispersants.

8. The pretreatment system of any of the preceding Aspects, wherein the metal of the metal sulfate salt comprises nickel, copper, zinc, iron, magnesium, cobalt, aluminum or combinations thereof, preferably nickel, cobalt or combinations thereof.

9. A method of treating a substrate comprising:

a) contacting at least a portion of a surface of the substrate with an activating rinse comprising a dispersion of metal phosphate particles having a D_{90} particle size of no greater than 10 μm, wherein the metal phosphate comprises divalent or trivalent metals or combinations thereof; and

b) contacting at least a portion of the surface that has been contacted with the activating rinse with a pretreatment composition comprising zinc ions and phosphate ions, wherein the pretreatment composition is substantially free of nickel.

10. The method of Aspect 9, wherein the D_{90} particle size is measured from a sample of the activating rinse that has been sonicated.

11. The method of Aspect 9 or 10, wherein the contacting with the pretreatment composition comprises immersing the substrate in a bath comprising pretreatment composition, wherein the bath temperature is 20 °C to 60 °C.

12. The method of Aspects 9 to 11, wherein the activating rinse further comprises a metal sulfate salt, wherein the metal of the metal sulfate salt comprises nickel, copper, zinc, iron, magnesium, cobalt, aluminum or combinations thereof, preferably nickel, cobalt or combinations thereof.

13. The method of any of Aspects 9 to 12, wherein the substrate is treated with the substrate pretreatment system according to any of Aspects 1 to 8.

14. A substrate treated with the pretreatment system of any of Aspects 1 to 8, preferably in a method according to any of Aspects 9 to 13.

15. The substrate of Aspect 13, wherein the phosphate coating formed from the pretreatment composition comprises metal/zinc phosphate crystals having an average crystal size of 0.4 μm to 2 μm, preferably of 0.7 μm to 1.5 μm as measured by a scanning electron microscope at 10,000x magnification.

16. The substrate of Aspects 14 or 15, wherein the phosphate coating has a weight of 4.4 g/m^2 or less and an exposed adhesion value of 6 or greater.

17. The substrate of any of Aspects 14 to 16, wherein the phosphate coating has a weight of 0.5 to 4 g/m^2 as measured by the weigh-strip-weigh method.

18. The substrate of any of Aspects 14 to 17, wherein the pretreatment composition has been applied from a pretreatment bath having a temperature of 20 °C to 60 °C.

19. The substrate of any of Aspects 14 to 18, wherein the substrate further comprises an electrodeposited layer.

We claim:

1. A substrate pretreatment system, comprising:

a) an activating rinse for treating at least a portion of a substrate comprising a dispersion of metal phosphate particles having a D_{90} particle size of no greater than 10 μm, wherein the metal phosphate comprises divalent or trivalent metals or combinations thereof; and

b) a pretreatment composition for treating at least a portion of the substrate treated with the activating rinse, comprising zinc ions and phosphate ions, wherein the pretreatment composition is substantially free of nickel.

2. The pretreatment system of Claim 1, wherein the activating rinse further comprises a metal sulfate salt, wherein the sulfate of the metal sulfate salt is present in an amount of 5 ppm to 5000 ppm based on a total weight of the activating rinse.

3. The pretreatment system of Claim 1, wherein the D_{90} particle size is measured from a sample of the activating rinse that has been sonicated.

4. The pretreatment system of Claim 1, wherein the metal phosphate particles have a D_{90} particle size of no more than 1 μm.

5. The pretreatment system of Claim 4, wherein the D_{90} particle size is measured from a sample of the activating rinse that has been sonicated.

6. The pretreatment system of Claim 1, wherein the metal phosphate particles have a D_{90} particle size of 50 nm to 500 nm.

7. The pretreatment system of Claim 1, wherein the divalent or trivalent metals of the metal phosphate in the activating rinse comprise zinc, iron or a combination thereof.

8. The pretreatment system of Claim 1, wherein the pretreatment composition is used in a pretreatment bath having a temperature of 20°C to 60°C.

9. The pretreatment system of Claim 1, wherein the metal of the metal sulfate salt comprises nickel, copper, zinc, iron, magnesium, cobalt, aluminum or combinations thereof.

10. The pretreatment system of Claim 1, wherein the metal of the metal sulfate salt comprises nickel, cobalt or combinations thereof.

11. A substrate treated with the pretreatment system of Claim 1.

12. The substrate of Claim 11, wherein the phosphate coating formed from the pretreatment composition comprises metal/zinc phosphate crystals having an average crystal size of 0.4 μm to 2 μm as measured by a scanning electron microscope at 10,000x magnification.

13. The substrate of Claim 11, wherein the phosphate coating formed from the pretreatment composition comprises metal/zinc crystals having an average crystal size of 0.7 μm to 1.5 μm as measured by a scanning electron microscope at 10,000x magnification.

15. The substrate of Claim 11, wherein the phosphate coating has a weight of 0.5 to 4 g/m^2 as measured by the weigh-strip-weigh method.

16. The substrate of Claim 11, wherein the phosphate coating has a weight of 4.4 g/m^2 or less and an exposed adhesion value of 6 or greater.

17. The substrate of Claim 11, wherein the D_{90} particle size is measured from a sample of the activating rinse that has been sonicated.

18. The substrate of Claim 11, further comprising an electrodeposited layer.

19. A method of treating a substrate comprising:

a) contacting at least a portion of a surface of the substrate with an activating rinse comprising a dispersion of metal phosphate particles having a D_{90} particle size of no greater than 10 μm, wherein the metal phosphate comprises divalent or trivalent metals or combinations thereof; and

b) contacting at least a portion of the surface that has been contacted with the activating rinse with a pretreatment composition comprising zinc ions and phosphate ions, wherein the pretreatment composition is substantially free of nickel.

20. The method of Claim 19, wherein the (b) contacting comprises immersing the substrate in a bath comprising the pretreatment composition, wherein the bath temperature is 20°C to 60°C.

21. The method of Claim 19, wherein the metal of the metal sulfate salt comprises nickel, copper, zinc, iron, magnesium, cobalt, aluminum or combinations thereof.

22. The method of Claim 19, wherein the metal of the metal sulfate salt comprises nickel, cobalt or combinations thereof.

23. The method of Claim 19, wherein the activating rinse further comprises a metal sulfate salt.

24. The substrate of Claim 19, wherein the D_{90} particle size is measured from a sample of the activating rinse that has been sonicated.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/029487

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C22/12 C23C22/78
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/12341 A1 (HENKEL CORP [US]; BANNAI HIROKATSU [JP]; NAGASHIMA YASUHIKO [JP]; NAKA) 22 February 2001 (2001-02-22) page 1, lines 1-24 page 2, line 4 - page 3, line 30 page 3, line 36 - page 5, line 18 page 6, line 19 - page 7, line 35 page 8, line 5 - page 10, line 31 page 11; example 4; table 1 page 15; example 4; table 5 page 16; example 11; table 7 page 19; example 11; table 10 page 20; example 16; table 12 page 23; example 16; table 15 page 24; example 21; table 17 page 27; example 21; table 20 ----- -/--	1,2,4, 7-11, 18-23

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer
Handrea-Haller, M

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International application No

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