Coating compositions exhibiting corrosion resistance properties, related coated substrates, and methods

Coating compositions are disclosed that include corrosion resisting particles such that the coating composition can exhibit corrosion resistance properties. Also disclosed are substrates at least partially coated with a coating deposited from such a composition and multi-component composite coatings, wherein at least one coating later is deposited from such a coating composition.
The present invention relates to coating compositions that comprise corrosion resisting particles such that the coating compositions exhibit corrosion resistance properties. The present invention also relates to substrates at least partially coated with a coating deposited from such a composition and multi-component composite coatings, wherein at least one coating layer is deposited from such a coating composition.

Coating systems that are deposited onto a substrate and cured, such as "color-plus-clear" and "monocoat" coating systems, can be subject to damage from the environment. For example, corrosion of a coated metallic substrate can occur as the substrate is exposed to oxygen and water present in the atmosphere. As a result, a "primer" coating layer is often used to protect the substrate from corrosion. The primer layer is often applied directly to a bare or pretreated metallic substrate. In some cases, particularly where the primer layer is to be applied over a bare metallic substrate, the primer layer is deposited from a composition that includes a material, such as an acid, such as phosphoric acid, which enhances the adhesion of the primer layer to the substrate. Such primers are sometimes known as "etch primers".

As indicated, in some cases metallic substrates are "pretreated" before a primer coating layer is applied (if such a primer coating is used). Such "pretreatments" often involve the application of a phosphate conversion coating, followed by a rinse, prior to the application of a protective or decorative coating. The pretreatment often acts to passivate the metal substrate and promotes corrosion resistance.

Historically, corrosion resistant "primer" coatings and metal pretreatments have utilized chromium compounds and/or other heavy metals, such as lead, to achieve a desired level of corrosion resistance and adhesion to subsequently applied coatings. For example, metal pretreatments often utilize phosphate conversion coating compositions that contain heavy metals, such as nickel, and post-rinses that contain chrome. In addition, the compositions used to produce a corrosion resistant "primer" coating often contain chromium compounds. An example of such a primer composition is disclosed in United States Patent No. 4,069,187. The use of chromium and/or other heavy metals, however, results in the production of waste streams that pose environmental concerns and disposal issues.

More recently, efforts have been made to reduce or eliminate the use of chromium and/or other heavy metals. As a result, coating compositions have been developed that contain other materials added to inhibit corrosion. These materials have included, for example, zinc phosphate, iron phosphate, zinc molybdate, and calcium molybdate particles, among others, and typically comprise particles having a particle size of approximately a micron or larger. The corrosion resistance capability of such compositions, however, has been inferior to their chrome containing counterparts.

As a result, it would be desirable to provide coating compositions that are substantially free of chromium and/or other heavy metals. As a result, coating compositions have been developed that contain other materials added to inhibit corrosion. These materials have included, for example, zinc phosphate, iron phosphate, zinc molybdate, and calcium molybdate particles, among others, and typically comprise particles having a particle size of approximately a micron or larger. The corrosion resistance capability of such compositions, however, has been inferior to their chrome containing counterparts.

The present invention relates to coating compositions that comprise corrosion resisting particles such that the coating compositions exhibit corrosion resistance properties. The present invention also relates to substrates at least partially coated with a coating deposited from such a composition and multi-component composite coatings, wherein at least one coating layer is deposited from such a coating composition.

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As a result, it would be desirable to provide coating compositions that are substantially free of chromium and/or other heavy metals. As a result, coating compositions have been developed that contain other materials added to inhibit corrosion. These materials have included, for example, zinc phosphate, iron phosphate, zinc molybdate, and calcium molybdate particles, among others, and typically comprise particles having a particle size of approximately a micron or larger. The corrosion resistance capability of such compositions, however, has been inferior to their chrome containing counterparts.

The present invention relates to coating compositions that comprise corrosion resisting particles such that the coating compositions exhibit corrosion resistance properties. The present invention also relates to substrates at least partially coated with a coating deposited from such a composition and multi-component composite coatings, wherein at least one coating layer is deposited from such a coating composition.

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As a result, it would be desirable to provide coating compositions that are substantially free of chromium and/or other heavy metals. As a result, coating compositions have been developed that contain other materials added to inhibit corrosion. These materials have included, for example, zinc phosphate, iron phosphate, zinc molybdate, and calcium molybdate particles, among others, and typically comprise particles having a particle size of approximately a micron or larger. The corrosion resistance capability of such compositions, however, has been inferior to their chrome containing counterparts.

The present invention relates to coating compositions that comprise corrosion resisting particles such that the coating compositions exhibit corrosion resistance properties. The present invention also relates to substrates at least partially coated with a coating deposited from such a composition and multi-component composite coatings, wherein at least one coating layer is deposited from such a coating composition.

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As a result, it would be desirable to provide coating compositions that are substantially free of chromium and/or other heavy metals. As a result, coating compositions have been developed that contain other materials added to inhibit corrosion. These materials have included, for example, zinc phosphate, iron phosphate, zinc molybdate, and calcium molybdate particles, among others, and typically comprise particles having a particle size of approximately a micron or larger. The corrosion resistance capability of such compositions, however, has been inferior to their chrome containing counterparts.
For purposes of the following detailed description, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

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.

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

In this application, the use of the singular includes the plural and plural encompasses singular, unless specifically stated otherwise. For example, and without limitation, this application refers to coating compositions that, in certain embodiments, comprise a "film-forming resin." Such references to "a film-forming resin" is meant to encompass coating compositions comprising one film-forming resin as well as coating compositions that comprise a mixture of two or more film-forming resins. 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.

In certain embodiments, the present invention is directed to coating compositions that are substantially free of chromium containing material. In other embodiments, the coating compositions of the present invention are completely free of such a material. As used herein, the term "substantially free" means that the material being discussed is present in the composition, if at all, as an incidental impurity. In other words, the material does not affect the properties of the composition. This means that, in certain embodiments of the present invention, the coating composition contains less than 2 weight percent of chromium containing material or, in some cases, less than 0.05 weight percent of chromium containing material, wherein such weight percents are based on the total weight of the composition. As used herein, the term "completely free" means that the material is not present in the composition at all. Thus, certain embodiments of the coating compositions of the present invention contain no chromium-containing material. As used herein, the term "chromium containing material" refers to materials that include a chromium trioxide group, CrO₃. Non-limiting examples of such materials include chromic acid, chromium trioxide, chromic acid anhydride, dichromate salts, such as ammonium dichromate, sodium dichromate, potassium dichromate, and calcium, barium, magnesium, zinc, cadmium, and strontium dichromate.

Certain embodiments of the coating compositions of the present invention are substantially free of other undesirable materials, including heavy metals, such as lead and nickel. In certain embodiments, the coating compositions of the present invention are completely free of such materials.

As indicated, the coating compositions of the present invention comprise "corrosion resisting particles." As used herein, the term "corrosion resisting particles" refers to particles which, when included in a coating composition that is deposited upon a substrate, act to provide a coating that resists or, in some cases, even prevents, the alteration or degradation of the substrate, such as by a chemical or electrochemical oxidizing process, including rust in iron containing substrates and degradative oxides in aluminum substrates.

The present invention is directed to coating compositions that comprise corrosion resisting particles comprising magnesium oxide (MgO).

Certain embodiments of the coating compositions of the present invention comprise ultrafine corrosion resisting particles. As used herein, the term "ultrafine" refers to particles that have a B.E.T. specific surface area of at least 10 square meters per gram, such as 30 to 500 square meters per gram, or, in some cases, 80 to 250 square meters per gram. As used herein, the term "B.E.T. specific surface area" refers to a specific surface area determined by nitrogen adsorption according to the ASTMD 3663-78 standard based on the Brunauer-Emmett-Teller method described in the periodical "The Journal of the American Chemical Society", 60, 309 (1938).

In certain embodiments, the coating compositions of the present invention comprise corrosion resisting particles having a calculated equivalent spherical diameter of no more than 200 nanometers, such as no more than 100 nanometers, or, in certain embodiments, 5 to 50 nanometers. As will be understood by those skilled in the art, a calculated equivalent spherical diameter can be determined from the B.E.T. specific surface area according to the following equation:
Certain embodiments of the coating compositions of the present invention comprise corrosion resisting particles having an average primary particle size of no more than 100 nanometers, such as no more than 50 nanometers, or, in certain embodiments, no more than 20 nanometers, as determined by visually examining a micrograph of a transmission electron microscopy ("TEM") image, measuring the diameter of the particles in the image, and calculating the average primary particle size of the measured particles based on magnification of the TEM image. One of ordinary skill in the art will understand how to prepare such a TEM image and determine the primary particle size based on the magnification and the Examples contained herein illustrate a suitable method for preparing a TEM image. The primary particle size of a particle refers to the smallest diameter sphere that will completely enclose the particle. As used herein, the term "primary particle size" refers to the size of an individual particle as opposed to an agglomeration of two or more individual particles.

In certain embodiments, the corrosion resisting particles have an affinity for the medium of the composition sufficient to keep the particles suspended therein. In these embodiments, the affinity of the particles for the medium is greater than the affinity of the particles for each other, thereby reducing or eliminating agglomeration of the particles within the medium.

The shape (or morphology) of the corrosion resisting particles can vary. For example, generally spherical morphologies can be used, as well as particles that are cubic, platy, or acicular (elongated or fibrous).

In certain embodiments, the ultrafine corrosion resisting particles that are included in certain embodiments of the coating compositions of the present invention may be prepared by various methods, including gas phase synthesis processes, such as, for example, flame pyrolysis, hot walled reactor, chemical vapor synthesis, among other methods.

The ultrafine corrosion resisting particles comprise a clay. In certain embodiments, such clays are treated with a lanthanide and/or transition metal salt. Suitable clays include, for example, layer structured Laponite® (a hydrous sodium lithium magnesium silicate modified with tetra sodium pyrophosphate commercially available from Southern Clay Products, Inc.) and bentonite (an aluminum phyllosilicate generally impure clay consisting mostly of montmorillonite, (Na,Ca)0.33(Al,Mg)2Si4O10(OH)2·nH2O).

Such corrosion resisting particles may be produced by adding a clay, such as the layer structured Laponite® referenced above, to a stirred dilute solution of a metal salt (up to 50% by weight metal), such as, for example, cerium acetate or zinc acetate, in water and filtering off the resulting solid precipitate. The solid precipitate may, if desired, be washed, such as with water and/or acetone, and dried.

In certain embodiments, the present invention is directed to coating compositions that comprise corrosion resisting particles comprising magnesium oxide in combination with a pH buffering agent, such as, for example, a borate.

As used herein, the term "pH buffering agent" is meant to refer to a material that adjusts the pH of the inorganic oxide to a level higher than the pH would be in the absence of the material. In certain embodiments, such corrosion resisting particles comprise a mixed metal oxide that includes borate (B₂O₃), and magnesium. In certain embodiments, such a mixed oxide is deposited on and/or within a support.

In certain embodiments, the corrosion resisting particles comprise magnesium oxide, a borate, and a silica support, such as fumed silica, commercially available under the tradename Aerosil® from Degussa, or precipitated silica, such as HiSil® T600 from PPG Industries, Pittsburgh, Pennsylvania. In certain embodiments, the support has an average primary particle size of no more than 20 nanometers. In certain embodiments, such corrosion resisting particles provide desirable protection against both edge corrosion and scribe-corrosion on the surface of a substrate that is exposed to anodic dissolution.

Specific non-limiting example of suitable corrosion resisting particles comprising a mixed metal oxide including borate comprises MgO·B₂O₃. Such corrosion resisting pigments can be produced, for example, by precipitating the such materials on the support. Such precipitation may be conducted by, for example, combining boric acid and one or more precursor materials comprising magnesium with a slurry of water and silica, evaporating the water, and then calcining the resulting material to produce the corrosion resisting particles, which may then be milled to a desired particle size.

In certain embodiments, the corrosion resisting particles may also comprise additional materials, such as phosphates, silicates, hydroxy-phosphates, and/or hydroxy-silicates of a metal, such as zinc or aluminum.

In certain embodiments, one or more of the previously described corrosion resisting particles are present in the coating compositions of the present invention in an amount of 3 to 50 percent by volume, such as 8 to 30 percent by volume, or, in certain embodiments, 10 to 18 percent by volume, wherein the volume percents are based on the total volume of the coating composition.

In certain embodiments, the coating compositions of the present invention comprise corrosion resisting particles comprising chemically modified particles having an average primary particle size of no more than 500 nanometers, in
some particles are described in United States Patent No. 6,790,904 at col. 3, line 43 to col. 8, line 46; United States Patent Application Publication No. 2003/0229157 A1 at [0021] to [0048]; United States Patent No. 6,835,458 at col. 4, line 54 to col. 7, line 58; and United States Patent No. 6,593,417 at col. 23, line 48 to col. 24, line 32, the cited portions of which being incorporated by reference herein. Suitable chemically modified particles are also commercially available, such as those available under the tradename NANOBYK-3650, from Byk-Chemie.

[0032] While such chemically modified particles are known in the art for providing mar and/or scratch resistance properties to coating compositions into which they are incorporated, the present inventors have surprisingly discovered that they also impart corrosion resistance properties to metal substrate primer compositions, such as etch-primer, and/or pretreatment coating compositions when such compositions are applied to a bare metal substrate. In fact, the inventors have discovered that, even when such chemically-modified particles are included in a coating composition in relatively small amounts, i.e., particle to film-forming binder weight ratios of less than 0.2, the coating composition, when deposited onto at least a portion of a bare metal substrate selected from cold rolled steel, electrogalvanized steel and aluminum and cured, sometimes produces a substrate that exhibits corrosion resistance properties similar to, or, in some cases, greater than, the corrosion resistance properties the same substrate exhibits when at least partially coated under the same conditions with a conventional chrome-containing corrosion-resistant composition (as described in more detail below). As a result, the inventors have discovered that such corrosion resistant particles can be used to replace chromium in metal substrate primer coating compositions, such as etch-primer, and/or metal pretreatment coating compositions.

[0033] As previously indicated, in certain embodiments, the coating compositions of the present invention comprise a 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.

[0034] Film-forming resins that may be used in the coating compositions of the present invention include, without limitation, those 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.

[0035] In certain embodiments, the film-forming resin included within the coating compositions of the present invention comprises a thermosetting film-forming resin. As used herein, the term "thermosetting" refers to resins that set irreversibly upon curing or crosslinking, wherein the polymer chains of the polymeric components are joined together by covalent bonds. This property is usually associated with a cross-linking reaction of the composition constituents often induced, for example, by heat or radiation. See Hawley, Gessner G., The Condensed Chemical Dictionary, Ninth Edition., page 856; Surface Coatings, vol. 2, Oil and Colour Chemists’ Association, Australia, TAFE Educational Books (1974). Curing or crosslinking reactions also may be carried out under ambient conditions. Once cured or crosslinked, a thermosetting resin will not melt upon the application of heat and is insoluble in solvents. In other embodiments, the film-forming resin included within the coating compositions of the present invention comprises a thermoplastic resin. As used herein, the term "thermoplastic" refers to resins that comprise polymeric components that are not joined by covalent bonds and thereby can undergo liquid flow upon heating and are soluble in solvents. See Saunders, K.J., Organic Polymer Chemistry, pp. 41-42, Chapman and Hall, London (1973).

[0036] Film-forming resins suitable for use in the coating compositions of the present invention include, for example, those formed from the reaction of a polymer having at least one type of reactive group and a curing agent having reactive groups reactive with the reactive group(s) of the polymer. As used herein, the term "polymer" is meant to encompass oligomers, and includes, without limitation, both homopolymers and copolymers. The polymers can be, for example, acrylic, saturated or unsaturated polyester, polyurethane or polyether, polyvinyl, cellulose, acrylate, silicon-based polymers, co-polymers thereof, and mixtures thereof, and can contain reactive groups such as epoxy, carboxylic acid, hydroxyl, isocyanate, amide, carbamate and carboxylate groups, among others, including mixtures thereof.

[0037] Suitable acrylic polymers include, for example, those described in United States Patent Application Publication 2003/0158316 A1 at [0030] - [0039], the cited portion of which being incorporated herein by reference. Suitable polyester polymers include, for example, those described in United States Patent Application Publication 2003/0158316 A1 at [0040] - [0046], the cited portion of which being incorporated herein by reference. Suitable polyurethane polymers include, for example, those described in United States Patent Application Publication 2003/0158316 A1 at [0047] - [0052], the cited portion of which being incorporated hereby by reference. Suitable silicon-based polymers are defined in United States Patent No. 6,623,791 at col. 9, lines 5-10, the cited portion of which being incorporated herein by reference.

[0038] In certain embodiments of the present invention, the film-forming resin comprises a polyvinyl polymer, such as a polyvinyl butyral resin. Such resins may be produced by reacting a polyvinyl alcohol with an aldehyde, such as acetaldehyde, formaldehyde, or butyraldehyde, among others. Polyvinyl alcohols may be produced by the polymerization of vinyl acetate monomer and the subsequent, alkaline-catalyzed methanolation of the polyvinyl acetate obtained. The acetalization reaction of polyvinyl alcohol and butyraldehyde is not quantitative, so the resulting polyvinyl butyral may
Commercially available polyvinyl butyral resins may be used. Such resins often have an average degree of polymerization of 500 to 1000 and a degree of buyration of 57 to 70 mole percent. Specific examples of suitable polyvinyl butyral resins include the MOWITAL® line of polyvinyl butyral resins commercially available from Kuraray America, Inc., New York, New York and the BUTVAR® polyvinyl butyral resins commercially available from Solutia Inc.

As indicated earlier, the term "cure" of composition components. As used herein, the term "cure" means that any crosslinkable components of the composition are at least partially crosslinked. In certain embodiments, the crosslink density of the crosslinkable components, i.e., the degree of crosslinking, ranges from 5 percent to 100 percent of complete crosslinking, such as 35 percent to 85 percent of complete crosslinking. One skilled in the art will understand that the presence and degree of crosslinking, i.e., the crosslink density, can be determined by a variety of methods, such as dynamic mechanical thermal analysis (DMTA) using a Polymer Laboratories MK III DMTA analyzer, as is described in United States Patent No. 6,803,408, at col. 7, line 66 to col. 8, line 18, the cited portion of which being incorporated herein by reference.

Any of a variety of curing agents known to those skilled in the art may be used. For example exemplary suitable aminoplast and phenoplast resins are described in United States Patent No. 3,919,351 at col. 5, line 22 to col. 6, line 25, the cited portion of which being incorporated herein by reference. Exemplary suitable polyisocyanates and blocked isocyanates are described in United States Patent No. 4,546,045 at col. 5, lines 16 to 38; and in United States Patent No. 5,468,802 at col. 3, lines 48 to 60, the cited portions of which being incorporated herein by reference. Exemplary suitable anhydrides are described in United States Patent No. 4,798,746 at col. 10, lines 16 to 50; and in United States Patent No. 4,732,790 at col. 3, lines 41 to 57, the cited portions of which being incorporated herein by reference. Exemplary suitable polyepoxides are described in United States Patent No. 4,681,811 at col. 5, lines 33 to 58, the cited portion of which being incorporated herein by reference. Exemplary suitable polyacids are described in United States Patent No. 4,681,811 at col. 6, line 45 to col. 9, line 54, the cited portion of which being incorporated herein by reference. Exemplary suitable polyols are described in United States Patent No. 4,046,729 at col. 7, line 52 to col. 8, line 9 and col. 8, line 29 to col. 9, line 66, and in United States Patent No. 3,919,315 at col. 2, line 64 to col. 3, line 33, the cited portions of which being incorporated herein by reference. Examples suitable polyamines described in United States Patent No. 4,046,729 at col. 6, line 61 to col. 7, line 26, and in United States Patent No. 3,799,854 at column 3, lines 13 to 50, the cited portions of which being incorporated herein by reference. Appropriate mixtures of curing agents, such as those described above, may be used.

In certain embodiments, the coating compositions of the present invention are formulated as a one-component composition where a curing agent is admixed with other composition components to form a storage stable composition. In other embodiments, compositions of the present invention can be formulated as a two-component composition where a curing agent is added to a pre-formed admixture of the other composition components just prior to application.

In certain embodiments, the film-forming resin is present in the coating compositions of the present invention in an amount greater than 30 weight percent, such as 40 to 90 weight percent, or, in some cases, 50 to 90 weight percent, with weight percent being based on the total weight of the coating composition. When a curing agent is used, it may, in certain embodiments, be present in an amount of up to 70 weight percent, such as 10 to 70 weight percent; this weight percent is also based on the total weight of the coating composition.

In certain embodiments, the coating compositions of the present invention are in the form of liquid coating compositions, examples of which include aqueous and solvent-based coating compositions and electrodepositable coating compositions. The coating compositions of the present invention may also be in the form of a co-reactable solid in particulate form, i.e., a powder coating composition. Regardless of the form, the coating compositions of the present invention may be pigmented or clear, and may be used alone or in combination as primers, basecoats, or topcoats. Certain embodiments of the present invention, as discussed in more detail below, are directed to corrosion resistant primer and/or pretreatment coating compositions. As indicated, certain embodiments of the present invention are directed to metal substrate primer coating compositions, such as "etch primers," and/or metal substrate pretreatment coating compositions. As used herein, the term "primer coating composition" refers to coating compositions from which an undercoating may be deposited onto a substrate in order to prepare the surface for application of a protective or decorative coating system. As used herein, the term "etch primer" refers to primer coating compositions that include an adhesion promoting component, such as a free acid as described in more detail below. As used herein, the term "pretreatment coating composition" refers to coating compositions that can be applied at very low film thickness to a bare substrate to improve corrosion resistance or to increase adhesion of subsequently applied coating layers. Metal substrates that may be coated with such compositions include, for example, substrates comprising steel (including electrogalvanized steel, cold rolled steel, hot-dipped galvanized steel, among others), aluminum, aluminum alloys, zinc-aluminum alloys, and aluminum plated steel. Substrates that may be coated with such compositions also may comprise more than one metal or metal alloy, in that the substrate may be a combination of two or more metal substrates assembled together, such as hot-dipped galvanized steel assembled with aluminum substrates.
The metal substrate primer coating compositions and/or metal substrate pretreatment coating compositions of the present invention may be applied to bare metal. By "bare" is meant a virgin material that has not been treated with any pretreatment compositions, such as, for example, conventional phosphating baths, heavy metal rinses, etc. Additionally, bare metal substrates being coated with the primer coating compositions and/or pretreatment coating compositions of the present invention may be a cut edge of a substrate that is otherwise treated and/or coated over the rest of its surface.

Before applying a primer coating composition of the present invention and/or a metal pretreatment composition of the present invention, the metal substrate to be coated may first be cleaned to remove grease, dirt, or other extraneous matter. Conventional cleaning procedures and materials may be employed. These materials could include, for example, mild or strong alkaline cleaners, such as those that are commercially available. Examples include BASE Phase Non-Phos or BASE Phase #6, both of which are available from PPG Industries, Pretreatment and Specialty Products. The application of such cleaners may be followed and/or preceded by a water rinse.

The metal surface may then be rinsed with an aqueous acidic solution after cleaning with the alkaline cleaner and before contact with a metal substrate primer coating composition and/or metal substrate pretreatment composition of the present invention. Examples of suitable rinse solutions include mild or strong acidic cleaners, such as the dilute nitric acid solutions commercially available.

As previously indicated, certain embodiments of the present invention are directed to coating compositions comprising an adhesion promoting component. As used herein, the term "adhesion promoting component" refers to any material that is included in the composition to enhance the adhesion of the coating composition to a metal substrate.

In certain embodiments of the present invention, such an adhesion promoting component comprises a free acid. As used herein, the term "free acid" is meant to encompass organic and/or inorganic acids that are included as a separate component of the compositions of the present invention as opposed to any acids that may be used to form a polymer that may be present in the composition. In certain embodiments, the free acid included within the coating compositions of the present invention is selected from tannic acid, gallic acid, phosphoric acid, phosphorous acid, citric acid, malonic acid, a derivative thereof, or a mixture thereof. Suitable derivatives include esters, amides, and/or metal complexes of such acids.

In certain embodiments, the free acid comprises an organic acid, such as tannic acid, i.e., tannin. Tannins are extracted from various plants and trees which can be classified according to their chemical properties as (a) hydrolyzable tannins, (b) condensed tannins, and (c) mixed tannins containing both hydrolyzable and condensed tannins. Tannins useful in the present invention include those that contain a tannin extract from naturally occurring plants and trees, and are normally referred to as vegetable tannins. Suitable vegetable tannins include the crude, ordinary or hot-water-soluble condensed vegetable tannins, such as Quebracho, mimosa, mangrove, spruce, hemlock, gabin, wattles, catechu, uranday, tea, larch, myrobalan, chestnut wood, divi-divi, valonia, summac, chinchona, oak, etc. These vegetable tannins are not pure chemical compounds with known structures, but rather contain numerous components including phenolic moieties such as catechol, pyrogallol, etc., condensed into a complicated polymeric structure.

In certain embodiments, the free acid comprises a phosphoric acid, such as a 100 percent orthophosphoric acid, superphosphoric acid or the aqueous solutions thereof, such as a 70 to 90 percent phosphoric acid solution.

In addition to or in lieu of such free acids, other suitable adhesion promoting components are metal phosphates, organophosphates, and organophosphonates. Suitable organophosphates and organophosphonates include those disclosed in United States Patent Nos. 6,440,580 at col. 3, line 24 to col. 6, line 22, 5,294,265 at col. 1, line 53 to col. 2, line 55, and 5,306,526 at col. 2, line 15 to col. 3, line 8, the cited portions of which being incorporated herein by reference. Suitable metal phosphates include, for example, zinc phosphate, iron phosphate, manganese phosphate, calcium phosphate, magnesium phosphate, cobalt phosphate, zinc-iron phosphate, zinc-manganese phosphate, zinc-calcium phosphate, including the materials described in United States Patent Nos. 4,941,930, 5,238,506, and 5,653,790.

In certain embodiments, the adhesion promoting component comprises a phosphatized epoxy resin. Such resins may comprise the reaction product of one or more epoxy-functional materials and one or more phosphorus-containing materials. Non-limiting examples of such materials, which are suitable for use in the present invention, are disclosed in United States Patent No. 6,159,549 at col. 3, lines 19 to 62, the cited portion of which being incorporated by reference herein.

In certain embodiments, the adhesion promoting component is present in the metal substrate primer coating compositions and/or the metal pretreatment coating composition in an amount ranging from 0.05 to 20 percent by weight, such as 3 to 15 percent by weight, with the percents by weight being based on the total weight of the composition.

As previously indicated, in certain embodiments, such as embodiments where the coating compositions of the present invention comprise a metal substrate primer coating composition and/or a metal pretreatment composition, the composition may also comprise a film-forming resin. In certain embodiments, the film-forming resin is present in such compositions in an amount ranging from 20 to 90 percent by weight, such as 30 to 80 percent by weight, with the percents by weight being based on the total weight of the composition.

In certain embodiments, the coating compositions of the present invention may also comprise additional optional...
ingredients, such as those ingredients well known in the art of formulating surface coatings. Such optional ingredients may comprise, for example, pigments, dyes, surface active agents, flow control agents, thixotropic agents, fillers, anti-gassing agents, organic co-solvents, catalysts, antioxidants, light stabilizers, UV absorbers and other customary auxiliaries. Any such additives known in the art can be used, absent compatibility problems. Non-limiting examples of these materials and suitable amounts include those described in United States Patent No. 4,220,679; 4,403,003; 4,147,769; and 5,071,904.

[0057] In certain embodiments, the coating compositions of the present invention also comprise, in addition to any of the previously described corrosion resisting particles, conventional non-chrome corrosion resisting particles. Suitable conventional non-chrome corrosion resisting particles include, but are not limited to, iron phosphate, zinc phosphate, calcium ion-exchanged silica, colloidal silica, synthetic amorphous silica, and molybdates, such as calcium molybdate, zinc molybdate, barium molybdate, strontium molybdate, and mixtures thereof. Suitable calcium ion-exchanged silica is commercially available from W. R. Grace & Co. as SHIELDEX® AC3 and/or SHIELDEX® C303. Suitable amorphous silica is available from W. R. Grace & Co. under the tradename SYLOID®. Suitable zinc hydroxyl phosphate is commercially available from Elementis Specialties, Inc. under the tradename NALZIN® 2.

[0058] These conventional non-chrome corrosion resisting pigments typically comprise particles having a particle size of approximately one micron or larger. In certain embodiments, these particles are present in the coating compositions of the present invention in an amount ranging from 5 to 40 percent by weight, such as 10 to 25 percent by weight, with the percents by weight being based on the total solids weight of the composition.

[0059] In certain embodiments, the present invention is directed to coating compositions comprising an adhesion promoting component, a phenolic resin and an alkoxysilane, in addition to any of the previously described corrosion resisting particles. Suitable phenolic resins include those resins prepared by the condensation of a phenol or an alkyl substituted phenol with an aldehyde. Exemplary phenolic resins include those described in United States Patent No. 6,774,168 at col. 2, lines 23 to 65, the cited portion of which being incorporated by reference herein. Suitable alkoxysilanes are described in United States Patent No. 6,774,168 at col. 2, lines 23 to 65, incorporated herein by reference, and include, for example, acryloxyalkoxysilanes, such as γ-acryloxypropyltrimethoxysilane and methacryloyloalkoxysilanes, such as γ-methacryloyloxypropyltrimethoxysilane. Such compositions may also include a solvent, rheological agent, and/or pigment, as described in United States Patent No. 6,774,168 at col. 3, lines 28 to 41, the cited portion of which being incorporated by reference herein.

[0060] The inventors have discovered that the corrosion resisting particles disclosed herein are particularly suitable for use in etch-primers, such as automotive refinish etch-primers and metal coil coating primers. As a result, certain embodiments of the present invention are directed to etch-primers comprising: (a) a film-forming resin, such as a polyvinyl resin; (b) an adhesion promoting component, such as a free acid; and (c) corrosion resisting particles of the type described herein. As used herein, the term "refinish" refers to the act of redoing, restoring or repairing the surface or finish of an article.

[0061] The coating compositions of the present invention may be prepared by any of a variety of methods. For example, in certain embodiments, the previously described corrosion resisting particles are added at any time during the formulation of a coating composition comprising a film-forming resin, so long as they form a stable suspension in a film-forming resin. Coating compositions of the present invention can be prepared by first blending a film-forming resin, the previously described corrosion resisting particles, and a diluent, such as an organic solvent and/or water, in a closed container that contains ceramic grind media. The blend is subjected to high shear stress conditions, such as by shaking the blend on a high speed shaker, until a homogeneous dispersion of particles remains suspended in the film-forming resin with no visible particle settle in the container. If desired, any mode of applying stress to the blend can be utilized, so long as sufficient stress is applied to achieve a stable dispersion of the particles in the film-forming resin.

[0062] The coating compositions of the present invention may be applied to a substrate by known application techniques, such as dipping or immersion, spraying, intermittent spraying, dipping followed by spraying, spraying followed by dipping, brushing, or by roll-coating. Usual spray techniques and equipment for air spraying and electrostatic spraying, either manual or automatic methods, can be used. While the coating compositions of the present invention can be applied to various substrates, such as wood, glass, cloth, plastic, foam, including elastomeric substrates and the like, in many cases, the substrate comprises a metal.

[0063] In certain embodiments of the coating compositions of the present invention, after application of the composition to the substrate, a film is formed on the surface of the substrate by driving solvent, i.e., organic solvent and/or water, out of the film by heating or by an air-drying period. Suitable drying conditions will depend on the particular composition and/or application, but in some instances a drying time of from about 1 to 5 minutes at a temperature of about 80 to 250°F (20 to 121°C) will be sufficient. More than one coating layer may be applied if desired. Usually between coats, the previously applied coat is flashed; that is, exposed to ambient conditions for 5 to 30 minutes. In certain embodiments, the thickness of the coating is from 0.05 to 5 mils (1.3 to 127 microns), such as 0.05 to 3.0 mils (1.3 to 76.2 microns). The coating composition may then be heated. In the curing operation, solvents are driven off and crosslinkable components of the composition, if any, are crosslinked. The heating and curing operation is sometimes carried out at a temperature in the range of from 160 to 350°F (71 to 177°C) but, if needed, lower or higher temperatures may be used.
Corrosion is measured by "scribe creep," which is defined as the total distance the corrosion has traveled across the coated substrate after exposure. The coated substrate is removed from the test chamber and evaluated for corrosion along the scribe. An aqueous salt solution is continuously misted onto the substrate. The chamber is maintained at a constant temperature. The coated substrate is scribed with a knife to expose the bare metal substrate. The scribed substrate is placed into a test chamber where an aqueous salt solution is continuously misted onto the substrate. The chamber is maintained at a constant temperature. The coated substrate is exposed to the salt spray environment for a specified period of time, such as 500 or 1000 hours. After exposure, the coated substrate is removed from the test chamber and evaluated for corrosion along the scribe. Corrosion is measured by "scribe creep," which is defined as the total distance the corrosion has traveled across the coated substrate.
In this application, when it is stated that a substrate "exhibits corrosion resistance properties greater than" another substrate, it means that the substrate exhibits less scribe creep (the corrosion travels across the scribe fewer millimeters) compared to the other substrate.

In certain embodiments, the corrosion resisting particles are present in the coating compositions of the present invention in an amount sufficient to result in a substrate exhibiting corrosion resistance properties at least 15% greater or, in some cases, at least 50% greater, than the corrosion resistance properties exhibited by the same substrate when at least partially coated under the same conditions with a similar coating composition that does not include the corrosion resisting particles.

As used herein, the term "the same conditions" means that a coating composition is (i) deposited on the substrate at the same or similar film thickness as the composition to which it is being compared, and (ii) cured under the same or similar cure conditions, such as cure temperature, humidity, and time, as the composition to which it is being compared. As used herein, the term "similar coating composition that does not include the corrosion resisting particles" means that a coating composition contains the same components in the same or similar amounts as the composition to which it is being compared, except that the corrosion resisting particles described herein, which are included in the coating compositions of the present invention, are not present and are replaced with conventional non-chrome corrosion resisting particles, such as NALZIN® 2 or SHIELDEX® AC3 (identified earlier).

In many cases, the coating compositions of the present invention, when deposited onto at least a portion of a metal substrate selected from cold rolled steel, electrogalvanized steel and aluminum and cured, produce a substrate that exhibits corrosion resistance properties similar to, or, in some cases, greater than, the corrosion resistance properties exhibited by the same substrate when at least partially coated under the same conditions with a conventional chrome-containing corrosion-resistant composition. In some cases, the coating compositions of the present invention, when deposited onto at least a portion of a cold rolled steel, electrogalvanized steel and aluminum substrate and cured, produce a substrate that exhibits corrosion resistance properties similar to, or, in some cases, greater than, the corrosion resistance properties the same two substrates exhibit when at least partially coated under the same conditions with a conventional chrome-containing corrosion-resistant composition.

As a result, certain embodiments of the present invention are directed to coating compositions that comprise corrosion resisting particles selected from magnesium oxide particles having an average particle size of no more than 100 nanometers, and wherein the corrosion resisting particles are present in the composition in an amount sufficient to result in a composition that, when deposited onto at least a portion of a metal substrate selected from cold rolled steel, electrogalvanized steel and aluminum and cured, produces a substrate that exhibits corrosion resistance properties similar to, or, in some embodiments, greater than, the corrosion resistance properties the same substrate exhibits when at least partially coated under the same conditions with a conventional chrome-containing corrosion-resistant composition. In certain embodiments, such corrosion resisting particles are present in the composition in an amount sufficient to result in a composition that, when deposited onto at least a portion of two metal substrates selected from cold rolled steel, electrogalvanized steel and aluminum and cured, produces a substrate that exhibits corrosion resistance properties similar to, or, in some embodiments, greater than, the corrosion resistance properties the same three substrates exhibit when at least partially coated under the same conditions with a conventional chrome-containing corrosion-resistant composition.

In this application, when it is stated that a substrate "exhibits corrosion resistance properties similar to" another substrate, it means that the substrate exhibits scribe creep as measured by ASTM B 117 as described above no more than 10% greater than the substrate to which it is being compared. As used herein, the term "conventional chrome-containing corrosion-resistant composition" refers to coating compositions commercially available from PPG Industries, Inc., Pittsburgh, PA, under the tradenames D8099 and DX1791.

As will be appreciated by those skilled in the art based on the foregoing description, certain embodiments of the present invention are directed to methods for enhancing the corrosion resistance of a metal substrate, such methods comprising coating at least a portion of the substrate with a primer and/or pretreatment coating composition that comprises (a) an adhesion promoting component, and (b) corrosion resisting particles selected from magnesium oxide particles having an average particle size of no more than 100 nanometers. In certain embodiments, such primer compositions are substantially free of chromium containing material and/or also comprise a film-forming resin, such as a polyvinyl polymer.
As will also be appreciated by the skilled artisan, certain embodiments of the present invention are directed to methods for enhancing the corrosion resistance of a metal substrate. The methods comprise coating at least a portion of the substrate with a primer and/or pretreatment coating composition that comprises (a) an adhesion promoting component, and (b) corrosion resisting particles selected from) magnesium oxide particles having an average primary particle size of no more than 100 nanometers.

Illustrating the invention are the following examples, which, however, are not to be considered as limiting the invention to their details. Unless otherwise indicated, all parts and percentages in the following examples, as well as throughout the specification, are by weight.

EXAMPLES

The following Particle Examples describe the preparation of corrosion resisting particles suitable for use in certain embodiments of the coating compositions of the present invention.

PARTICLE EXAMPLE 1

A reaction flask was equipped with a stirrer, thermocouple and a condenser. Charge A and charge B (see table 1) were added and stirred for 15 minutes. Then, Charge C (see Table 1) was added over 5 minutes and stirred for 30 minutes. Then, 300 grams of water was added and heated to 40°C. The reaction mixture was stirred at 40°C for six hours and then cooled to ambient temperature. The solid precipitated was filtered off, washed with acetone and dried at ambient temperature for 24 hours.

PARTICLE EXAMPLE 2

A reaction flask was equipped with a stirrer, thermocouple and a condenser. Charge A and charge B (see Table 1) were added and stirred for 6 minutes. Then, 300 grams of water was added and heated to 40°C. The reaction mixture was stirred at 40°C for 375 minutes and then cooled to ambient temperature. The solid precipitated was filtered off, washed with acetone and dried at ambient temperature for 24 hours.

PARTICLE EXAMPLE 3

A reaction flask was equipped with a stirrer, thermocouple and a condenser. Charge A and charge B (see Table 1) were added and stirred for 32 minutes. Then, Charge C (see Table 1) was added over 5 minutes and stirred for 32 minutes. Then, 200 grams of water was added and heated to 40°C. The reaction mixture was stirred at 40°C for six hours and then cooled to ambient temperature. Then, five grams of triethylamine in 30 grams of water was added and stirred for an hour. The solid precipitated was filtered off, washed with acetone and dried at ambient temperature for 24 hours.

PARTICLE EXAMPLE 4

A reaction flask was equipped with a stirrer, thermocouple and a condenser. Charge A and charge B (see Table 1) were added and stirred for 45 minutes. Then, Charge C (see Table 1) was added over 5 minutes and stirred for 30 minutes. Then, 200 grams of water was added and heated to 40°C. The reaction mixture was stirred at 40°C for two hours. Then, charge D, sparged with nitrogen stream continuously, (see Table 1) was added over thirty minutes and stirred at 40°C for two hours. Reaction mixture was cooled to ambient temperature and nine grams of triethylamine were added, and stirred for 90 minutes. The solid precipitated was filtered off, washed with acetone and dried at ambient temperature for 24 hours.

PARTICLE EXAMPLE 5

A reaction flask was equipped with a stirrer, thermocouple and a condenser. Charge A and charge B (see Table 1) were added and stirred for 85 minutes. The temperature was raised to 75°C and stirred at 75°C for 55 minutes. Then, the reaction mixture was cooled to 50°C and Charge C (see Table 1) was added over 5 minutes and stirred for 25 minutes. Then, charge D, sparged with nitrogen stream continuously during addition, (see Table 1) was added over thirty minutes and stirred at 50°C for 375 minutes. The reaction mixture was cooled to ambient temperature and the solid precipitated was filtered off, washed with acetone and dried at ambient temperature for 24 hours.
A reaction flask was equipped with a stirrer, thermocouple and a condenser. Charge A and charge B (See Table 3) were added and stirred for 30 minutes. Then, the temperature was raised to 50°C and stirred for 105 minutes. Then, 100 grams of water was added and the reaction mixture was heated to 60°C and stirred for 45 minutes. Then, the heat source was removed. At a reaction temperature of 34°C, charge C (See Table 3) was added over five minutes. The reaction mixture was stirred for 30 minutes at 30°C. Charge D, sparged with nitrogen stream continuously during addition, (See Table 3) was added over thirty minutes and stirred at 30°C for 260 minutes. The reaction mixture was cooled to ambient temperature and the solid precipitated was filtered off, washed with acetone and dried at ambient conditions for 24 hours.

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Particle Example 1</th>
<th>Particle Example 2</th>
<th>Particle Example 3</th>
<th>Particle Example 4</th>
<th>Particle Example 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge A (grams)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deionized water</td>
<td>200.0</td>
<td>200.0</td>
<td>200.0</td>
<td>200.0</td>
<td>800</td>
</tr>
<tr>
<td>Charge B (grams)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cerium(III) acetate 1.5H₂O¹</td>
<td>34.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>102.0</td>
</tr>
<tr>
<td>Yttrium acetate Hydrate²</td>
<td>0.0</td>
<td>26.3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Manganese acetate 4H₂O³</td>
<td>0.0</td>
<td>0.0</td>
<td>24.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Zirconium sulfate⁴</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>27.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Zinc acetate dihydrate⁵</td>
<td>22.0</td>
<td>22.0</td>
<td>22.0</td>
<td>22.0</td>
<td>66.0</td>
</tr>
<tr>
<td>Charge C (grams)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silquest TEOS pure silane⁶</td>
<td>48.0</td>
<td>48.0</td>
<td>48.0</td>
<td>48.0</td>
<td>144.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>200.0</td>
<td>200.0</td>
<td>200.0</td>
<td>200.0</td>
<td>600.0</td>
</tr>
<tr>
<td>Charge D (grams)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethylamine⁷</td>
<td></td>
<td></td>
<td></td>
<td>5.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Deionized water</td>
<td></td>
<td></td>
<td></td>
<td>50.0</td>
<td>180.0</td>
</tr>
</tbody>
</table>

¹ Available from Prochem Inc.,
² Available from Aldrich
³ Available from Aldrich
⁴ Available from ICN Biomedicals Inc
⁵ Available from Barker Industries
⁶ Available from GE silicones
⁷ Available from Aldrich

PARTICLE EXAMPLE 11

[0085] A reaction flask was equipped with a stirrer, thermocouple and a condenser. Charge A and charge B (See Table 3) were added and stirred for 30 minutes. Then, the temperature was raised to 50°C and stirred for 105 minutes. Then, 100 grams of water was added and the reaction mixture was heated to 60°C and stirred for 45 minutes. Then, the heat source was removed. At a reaction temperature of 34°C, charge C (See Table 3) was added over five minutes. The reaction mixture was stirred for 30 minutes at 30°C. Charge D, sparged with nitrogen stream continuously during addition, (See Table 3) was added over thirty minutes and stirred at 30°C for 260 minutes. The reaction mixture was cooled to ambient temperature and the solid precipitated was filtered off, washed with acetone and dried at ambient conditions for 24 hours.
TABLE 3

<table>
<thead>
<tr>
<th>Charge A (grams)</th>
<th>Deionized water</th>
<th>200.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge B (grams)</td>
<td>Cerium (III) acetate 1.5H₂O</td>
<td>34.0</td>
</tr>
<tr>
<td></td>
<td>Zinc acetate dihydrate²</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>Magnesium(II)acetate.4H₂O³</td>
<td>21.2</td>
</tr>
<tr>
<td>Charge C (grams)</td>
<td>Silquest TEOS pure silane⁴</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>200.0</td>
</tr>
<tr>
<td></td>
<td>Phosphoric acid 85%⁵</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Sodium metasilicate⁶</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Deionized water</td>
<td>0.0</td>
</tr>
<tr>
<td>Charge D (grams)</td>
<td>Triethylamine⁷</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>Deionized water</td>
<td>60.0</td>
</tr>
</tbody>
</table>

¹ Available from Prochem Inc.,  
² Available from Barker Industries  
³ Available from Acros Organics  
⁴ Available from GE silicones  
⁵ Available from Fisher Scientific  
⁶ Available from Aldrich  
⁷ Available from Fisher Scientific

COATING COMPOSITION EXAMPLES 1A TO 1B

[0086] Coating compositions were prepared using the components and weights (in grams) shown in Table 50. All materials in the A pack of the formulation, were added under agitation with a Cowles blade in the order listed up to ethanol. 17.42 grams of ethanol was held out from the total until later in the preparation. Next, the poly(vinyl butyral) resin was slowly added while still under agitation and left to mix for 15 minutes. Epoxy resin was then added. Next, corrosion resisting particles, if any, and pigment(s) were added with heavy mixing for about ten minutes. Then, the rest of the ethanol and other solvents were slowly added. This final mixture was allowed to mix for ten minutes and was then added to a sealed 8 ounce glass container containing approximately 150 grams of the above material to approximately 125 grams of zircoa beads. This sealed container was then left on a paint shaker for two to 4 hours. After removing the paste from the paint shaker, the milling beads were filtered out with a standard paint filter and the finished material was ready.

[0087] The B pack of the formulation was prepared by adding the components to a suitable vessel under agitation with a paddle blade and allowing to mix for 20 minutes. When ready to spray, the two compositions were mixed.

TABLE 50

<table>
<thead>
<tr>
<th>Pack</th>
<th>Material</th>
<th>Example 1A</th>
<th>Example 1B</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>DOWANOL PM¹</td>
<td>9.18</td>
<td>9.18</td>
</tr>
<tr>
<td>A</td>
<td>BLS-2700²</td>
<td>10.17</td>
<td>10.17</td>
</tr>
<tr>
<td>A</td>
<td>Ethanol³</td>
<td>56.51</td>
<td>56.51</td>
</tr>
<tr>
<td>A</td>
<td>Butvar B-90⁴</td>
<td>6.9</td>
<td>6.9</td>
</tr>
<tr>
<td>A</td>
<td>EPON 834-X-80⁵</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>A</td>
<td>Particle Example 5</td>
<td>-</td>
<td>2.26</td>
</tr>
</tbody>
</table>
The compositions of Table 50, as well as Example 1G (described below), were applied to the test substrates identified in Table 51. The substrates were prepared by first cleaning with a wax and greaser remover (DX330, commercially available from PPG Industries, Inc.) and allowed to dry. The panels were then sanded with 180 grit using a DA orbital sander and again cleaned with DX330. The compositions were applied using a DeVilbiss GTI HVLP spray gun with a 1.4 spray tip, N2000 Cap, and 30 psi at gun. Each composition was applied in two coats with a five-minute flash in between to film builds of 0.50 to approximately 1.25 mils (12.7 to 31.8 microns). A minimum of twenty to thirty minutes and no more than one hour of time was allowed to elapse before applying a PPG Industries, Inc. global sealer D 839 over each composition. The sealer was mixed and applied as a wet-on-wet sealer to approximately 1.0 to 2.0 mils (25.4 to 50.8 microns) of paint and allowed to flash forty-five minutes before applying base coat. Deltron DBC base coat, commercially available from PPG Industries, Inc., was applied over the sealer in two coats with five to ten minutes flash time between coats to a film build thickness of approximately 0.5 mils (12.7 microns). The base coat was allowed approximately fifteen minutes time to flash before applying D893 Global clear coat, commercially available from PPG Industries, Inc., in two coats with five to ten minutes to flash between coats to a film build of 2.50 to 3.00 mils (63.5 to 76.2 microns). Sealer, base coat, and clear coat were mixed as the procedure for these products recommended by PPG Industries, Inc. Salt spray resistance was tested as described in ASTM B 117. Panels removed from salt spray testing after 1000 hours were measured for scribe creep across the scribe. Scribe creep values were reported as an average of six (6) measurements. Results are illustrated in Table 51, with lower value indicated better corrosion resistance results.

<table>
<thead>
<tr>
<th>Pack</th>
<th>Material</th>
<th>Example 1A</th>
<th>Example 1B</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>K-White G1056</td>
<td>2.26</td>
<td>2.26</td>
</tr>
<tr>
<td>A</td>
<td>Aerosil 200</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>A</td>
<td>Toluene</td>
<td>6.91</td>
<td>6.91</td>
</tr>
<tr>
<td>A</td>
<td>Xylene</td>
<td>5.19</td>
<td>5.19</td>
</tr>
<tr>
<td>A</td>
<td>Isobutyl Alcohol</td>
<td>5.89</td>
<td>5.89</td>
</tr>
<tr>
<td>B</td>
<td>Ethanol</td>
<td>85.28</td>
<td>85.28</td>
</tr>
<tr>
<td>B</td>
<td>Butanol</td>
<td>9.43</td>
<td>9.43</td>
</tr>
<tr>
<td>B</td>
<td>Phosphoric Acid 85%</td>
<td>1.59</td>
<td>1.59</td>
</tr>
<tr>
<td>B</td>
<td>Deionized Water</td>
<td>0.09</td>
<td>0.09</td>
</tr>
</tbody>
</table>

1 Propylene glycol monomethyl ether commercially available from BASF Corp.
2 Phenolic resin commercially available from Georgia Pacific
3 Organic solvent commercially available from ChemCentral Corp.
4 Poly (vinyl butyril) resin commercially available from Solutia Inc.
5 Epichlorohydin-Bisphenol A resin commercially available from Resolution Performance Products
6 Aluminum triphosphate compound commercially available from Tayca
7 Silicon dioxide commercially available from Cabot Corp.
8 Commercially available from Ashland Chemical Co.
9 Commercially available from Ashland Chemical Co.
10 Commercially available from Avecia.
11 Commercially available from BASF Corp.
12 Commercially available from Akzo Chemicals Inc.

Test Substrates

[0088] The compositions of Table 50, as well as Example 1G (described below), were applied to the test substrates identified in Table 51. The substrates were prepared by first cleaning with a wax and greaser remover (DX330, commercially available from PPG Industries, Inc.) and allowed to dry. The panels were then sanded with 180 grit using a DA orbital sander and again cleaned with DX330. The compositions were applied using a DeVilbiss GTI HVLP spray gun with a 1.4 spray tip, N2000 Cap, and 30 psi at gun. Each composition was applied in two coats with a five-minute flash in between to film builds of 0.50 to approximately 1.25 mils (12.7 to 31.8 microns). A minimum of twenty to thirty minutes and no more than one hour of time was allowed to elapse before applying a PPG Industries, Inc. global sealer D 839 over each composition. The sealer was mixed and applied as a wet-on-wet sealer to approximately 1.0 to 2.0 mils (25.4 to 50.8 microns) of paint and allowed to flash forty-five minutes before applying base coat. Deltron DBC base coat, commercially available from PPG Industries, Inc., was applied over the sealer in two coats with five to ten minutes flash time between coats to a film build thickness of approximately 0.5 mils (12.7 microns). The base coat was allowed approximately fifteen minutes time to flash before applying D893 Global clear coat, commercially available from PPG Industries, Inc., in two coats with five to ten minutes to flash between coats to a film build of 2.50 to 3.00 mils (63.5 to 76.2 microns). Sealer, base coat, and clear coat were mixed as the procedure for these products recommended by PPG Industries, Inc. Salt spray resistance was tested as described in ASTM B 117. Panels removed from salt spray testing after 1000 hours were measured for scribe creep across the scribe. Scribe creep values were reported as an average of six (6) measurements. Results are illustrated in Table 51, with lower value indicated better corrosion resistance results.
Coating compositions were prepared using the components and weights (in grams) shown in Table 58. Coatings were prepared in the same manner as described for Coating Composition Examples 1A to 1B.

### TABLE 51

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Example 1A</th>
<th>Example 1B</th>
<th>Example 1G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Rolled Steel (APR10288)</td>
<td>4.3</td>
<td>11.1</td>
<td>0</td>
</tr>
<tr>
<td>G-60 Galvanized (APR18661)</td>
<td>7.2</td>
<td>3.3</td>
<td>0</td>
</tr>
<tr>
<td>Aluminum (APR21047)</td>
<td>10.5</td>
<td>Delaminated</td>
<td>0</td>
</tr>
</tbody>
</table>


### TABLE 58

<table>
<thead>
<tr>
<th>Pack</th>
<th>Material</th>
<th>Example 5A</th>
<th>Example 5B</th>
<th>Example 5C</th>
<th>Example 5D</th>
<th>Example 5E</th>
<th>Example 5F</th>
<th>Example 5G</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>DOWANOL PM¹</td>
<td>9.18</td>
<td>9.18</td>
<td>9.18</td>
<td>9.18</td>
<td>9.18</td>
<td>9.18</td>
<td>9.18</td>
</tr>
<tr>
<td>A</td>
<td>Ethanol³</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
</tr>
<tr>
<td>A</td>
<td>Butvar B-90⁴</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
</tr>
<tr>
<td>A</td>
<td>Zinc chromate¹⁶</td>
<td>2.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>Magnesium Oxide¹⁷</td>
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<td>2.26</td>
<td>-</td>
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</tr>
<tr>
<td>A</td>
<td>Particle Example 1</td>
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<td>Particle Example 2</td>
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<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Particle Example 4</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>2.26</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Nalzin-2¹⁸</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.26</td>
</tr>
<tr>
<td>A</td>
<td>Aerosil 200⁷</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>A</td>
<td>Toluene⁸</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
</tr>
<tr>
<td>A</td>
<td>Xylene⁹</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
</tr>
<tr>
<td>A</td>
<td>Isobutyl Alcohol¹⁰</td>
<td>5.89</td>
<td>5.89</td>
<td>5.89</td>
<td>5.89</td>
<td>5.89</td>
<td>5.89</td>
<td>5.89</td>
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<tr>
<td>B</td>
<td>Ethanol³</td>
<td>85.28</td>
<td>85.28</td>
<td>85.28</td>
<td>85.28</td>
<td>85.28</td>
<td>85.28</td>
<td>85.28</td>
</tr>
<tr>
<td>B</td>
<td>Butanol¹¹</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
</tr>
<tr>
<td>B</td>
<td>Phosphoric Acid 85%¹²</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
</tr>
</tbody>
</table>
The compositions of Table 58, as well as Examples 5H and 5I (described below), were applied to the test substrates identified in Table 59 using the same procedure as was described above for Coating Composition Examples 1A, 1B and 1G. Results are illustrated in Table 59, with lower value indicated better corrosion resistance results.

**TABLE 59**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ex. 5A</th>
<th>Ex. 5B</th>
<th>Ex. 5C</th>
<th>Ex. 5D</th>
<th>Ex. 5E</th>
<th>Ex. 5F</th>
<th>Ex. 5G</th>
<th>Ex. 5H&lt;sup&gt;15&lt;/sup&gt;</th>
<th>Ex. 5I&lt;sup&gt;14&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Rolled Steel (APR10288)</td>
<td>6.2</td>
<td>4</td>
<td>0.7</td>
<td>1.3</td>
<td>3.3</td>
<td>0</td>
<td>13</td>
<td>10.7</td>
<td>8.2</td>
</tr>
<tr>
<td>G-60 Galvanized (APR18661)</td>
<td>10.7</td>
<td>5.2</td>
<td>15.2</td>
<td>13.2</td>
<td>11.8</td>
<td>14.3</td>
<td>15.6</td>
<td>10</td>
<td>7.8</td>
</tr>
<tr>
<td>Aluminum (APR21047)</td>
<td>Delam.</td>
<td>1</td>
<td>Delam.</td>
<td>Delam.</td>
<td>Delam.</td>
<td>Delam.</td>
<td>Delam.</td>
<td>6.2</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>15</sup> DPX-171 commercially available from PPG Industries, Inc., Pittsburgh, PA.

**COATING COMPOSITION EXAMPLES 6A TO 6H**

Coating compositions were prepared using the components and weights (in grams) shown in Table 60. Coatings were prepared in the same manner as described for Coating Composition Examples 1A to 1B.
## TABLE 60

<table>
<thead>
<tr>
<th>Pack</th>
<th>Material</th>
<th>Example 6A</th>
<th>Example 6B</th>
<th>Example 6C</th>
<th>Example 6D</th>
<th>Example 6E</th>
<th>Example 6F</th>
<th>Example 6G</th>
<th>Example 6H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ethanol³</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
<td>56.51</td>
</tr>
<tr>
<td>A</td>
<td>Butvar B-90⁴</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
<td>6.9</td>
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<tr>
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<td>EPON 834-X-8⁵⁵</td>
<td>3</td>
<td>-</td>
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<td>-</td>
<td>3</td>
<td>-</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>A</td>
<td>Magnesium Oxide¹⁷</td>
<td>-</td>
<td>2.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.26</td>
<td>2.26</td>
<td>2.26</td>
</tr>
<tr>
<td>A</td>
<td>Particle Example 1</td>
<td>-</td>
<td>-</td>
<td>2.26</td>
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<td>2.26</td>
<td>2.26</td>
<td>-</td>
<td>2.26</td>
</tr>
<tr>
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<td>Particle Example 11</td>
<td>2.26</td>
<td>2.26</td>
<td>-</td>
<td>2.26</td>
<td>-</td>
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<tr>
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<td>K-White G105⁸</td>
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<td>-</td>
<td>2.26</td>
<td>2.26</td>
<td>2.26</td>
<td>2.26</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Aerosil 200⁷</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>A</td>
<td>Toluene⁸</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
</tr>
<tr>
<td>A</td>
<td>Xylene⁹</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
<td>5.18</td>
</tr>
<tr>
<td>A</td>
<td>Isobutyl Alcohol¹⁰</td>
<td>5.89</td>
<td>5.89</td>
<td>5.89</td>
<td>5.89</td>
<td>5.89</td>
<td>5.89</td>
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<tr>
<td>B</td>
<td>Ethanol³</td>
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<td>85.28</td>
<td>85.28</td>
<td>85.28</td>
<td>85.28</td>
<td>85.28</td>
<td>85.28</td>
<td>85.28</td>
</tr>
<tr>
<td>B</td>
<td>Butanol¹¹</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
<td>9.43</td>
</tr>
<tr>
<td>B</td>
<td>Phosphoric Acid 85%¹²</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
</tr>
<tr>
<td>B</td>
<td>Deionized Water</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
</tbody>
</table>
The compositions of Table 60, as well as Examples 6I and 6J (described below), were applied to the test substrates identified in Table 61 using the same procedure as was described above for Coating Composition Examples 1A, 1B and 1G. Results are illustrated in Table 61, with lower value indicated better corrosion resistance results.

### TABLE 61

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ex. 6A</th>
<th>Ex. 6B</th>
<th>Ex. 6C</th>
<th>Ex. 6D</th>
<th>Ex. 6E</th>
<th>Ex. 6F</th>
<th>Ex. 6G</th>
<th>Ex. 6H</th>
<th>Ex. 6I</th>
<th>Ex. 6J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Rolled Steel</td>
<td>2.1</td>
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<td>0</td>
<td>0</td>
<td>0.5</td>
<td>13.7</td>
<td>24.2</td>
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</tr>
<tr>
<td>APR10288</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G-60 Galvanized Steel</td>
<td>7.3</td>
<td>3.2</td>
<td>4.4</td>
<td>2.6</td>
<td>2.7</td>
<td>0.5</td>
<td>0.7</td>
<td>0.5</td>
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<td>0</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
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<td>0</td>
<td>Delam.</td>
<td>Delam.</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The aspects of the invention are:

1. A primer and/or pretreatment coating composition comprising:
   - (a) an adhesion promoting component; and
   - (b) corrosion resisting particles selected from:
     - (i) magnesium oxide particles having an average primary particle size of no more than 100 nanometers;
     - (ii) particles comprising an inorganic oxide network comprising one or more inorganic oxides; and/or
     - (iii) chemically modified particles having an average primary particle size of no more than 500 nanometers.

2. The primer and/or pretreatment coating composition of aspect 1, wherein the composition is an etch primer.
3. The primer and/or pretreatment coating composition of aspect 1, wherein the composition is substantially free of chromium containing material.
4. The primer and/or pretreatment coating composition of aspect 1, wherein the magnesium oxide particles have an average particle size of no more than 50 nanometers.
5. The primer and/or pretreatment coating composition of aspect 1, wherein the particles comprising an inorganic oxide network comprising one or more inorganic oxides are formed from hydrolysis of metal salts.
6. The primer and/or pretreatment coating composition of aspect 1, wherein the particles comprising an inorganic oxide network comprising one or more inorganic oxides comprise cerium, zinc, zirconium and/or manganese.
7. The primer and/or pretreatment coating composition of aspect 6, wherein the particles comprising an inorganic oxide network comprising one or more inorganic oxides further comprises silicon.
8. The primer and/or pretreatment coating composition of aspect 1, wherein the particles comprising an inorganic oxide network comprising one or more inorganic oxides are ultrafine particles.
9. The primer and/or pretreatment coating composition of aspect 1, wherein the chemically modified particles are chemically modified by reaction of the particles with a compound of the formula:

F-L-Z

wherein F is a moiety containing one or more functional groups that will react with the particle surface, Z is a surface-active moiety that decreases the surface tension of the particle, and L is a group that links F and Z.
10. The primer and/or pretreatment coating composition of aspect 1, further comprising a film-forming resin.
11. The primer and/or pretreatment coating composition of aspect 10, wherein the weight ratio of the chemically modified particles to the film-forming resin in the composition is less than 0.2 and the composition, when deposited onto at least a portion of a metal substrate selected from cold rolled steel, electrogalvanized steel and aluminum and cured, produces a substrate that exhibits corrosion resistance properties at least similar to the corrosion resistance properties the same substrate exhibits when at least partially coated under the same conditions with a con-
ventional chrome-containing corrosion-resistant composition.

12. The primer and/or pretreatment coating composition of aspect 10, wherein the film-forming resin comprises a polyvinyl polymer.

13. The primer and/or pretreatment coating composition of aspect 1, wherein the adhesion promoting component comprises a free acid and/or a phosphatized epoxy resin.

14. The primer and/or pretreatment coating composition of aspect 1, wherein the composition further comprises a phenolic resin and an alkoxysilane.

15. The primer and/or pretreatment coating composition of aspect 1, wherein the composition further comprises corrosion resisting particles comprising a clay.

16. A metal substrate at least partially coated with the primer and/or pretreatment coating composition of aspect 1.

17. A method for improving the corrosion resistance properties of a primer and/or pretreatment coating composition, comprising including in the composition corrosion resisting particles selected from: (i) magnesium oxide particles having an average primary particle size of no more than 100 nanometers; (ii) particles comprising an inorganic oxide network comprising one or more inorganic oxide; and/or (iii) chemically modified particles having an average primary particle size of no more than 500 nanometers, such that the corrosion resistant particles are present in the composition in an amount sufficient to result in a composition that, when deposited onto at least a portion of one metal substrate selected from cold rolled steel, electrogalvanized steel and aluminum and cured, provides a substrate that exhibits corrosion resistance properties at least similar to the corrosion resistance properties that the same substrate exhibits when at least partially coated under the same conditions with a conventional chrome-containing corrosion-resistant composition.

18. A method for enhancing the corrosion resistance of a metal substrate, comprising coating at least a portion of a bare metal substrate with a primer and/or pretreatment coating composition that comprises: (a) an adhesion promoting component, and (b) corrosion resisting particles selected from: (i) magnesium oxide particles having an average primary particle size of no more than 100 nanometers; (ii) particles comprising an inorganic oxide network comprising one or more inorganic oxide; and/or (iii) chemically modified particles having an average primary particle size of no more than 500 nanometers.

19. A coating composition comprising:

(1) an adhesion promoting component, and

(2) corrosion resisting particles having a calculated equivalent spherical diameter of no more than 200 nanometers and comprising a plurality of inorganic oxides.

20. The coating composition of aspect 19, wherein at least one inorganic oxide comprises zinc, cerium, yttrium, magnesium, molybdenum, lithium, aluminum, tin, or calcium.

21. The coating composition of aspect 19, wherein the corrosion resisting particles are selected from (i) particles comprising oxides of cerium, zinc, and silicon; (ii) particles comprising oxides of calcium, zinc and silicon; (iii) particles comprising oxides of phosphorous, zinc and silicon; (iv) particles comprising oxides of yttrium, zinc, and silicon; (v) particles comprising oxides of molybdenum, zinc, and silicon; (vi) particles comprising oxides of boron, zinc, and silicon; (vii) particles comprising oxides of cerium, aluminum, and silicon, (viii) particles comprising oxides of magnesium or tin and silica, and (viii) particles comprising oxides of cerium, boron, and silicon, or a mixture thereof.

22. The coating composition of aspect 21, wherein the corrosion resisting particles comprise oxides of cerium, zinc, and silicon.

23. The coating composition of aspect 19, wherein the composition is substantially free of chromium containing material.

24. The coating composition of aspect 19, wherein the corrosion resisting particles are substantially free of zirconium.

25. The coating composition of aspect 19, wherein the corrosion resisting particles are selected from particles comprising:

(i) 10 to 25 percent by weight zinc oxide, 0.5 to 25 percent by weight cerium oxide, and 50 to 89.5 percent by weight silica;

(ii) 10 to 25 percent by weight zinc oxide, 0.5 to 25 percent by weight calcium oxide, and 50 to 89.5 percent by weight silica;

(iii) 10 to 25 percent by weight zinc oxide, 0.5 to 25 percent by weight yttrium oxide, and 50 to 89.5 percent by weight silica;

(iv) 10 to 25 percent by weight zinc oxide, 0.5 to 50 percent by weight phosphorous oxide, and 25 to 89.5 percent by weight silica;

(v) 10 to 25 percent by weight zinc oxide, 0.5 to 50 percent by weight boron oxide, and 25 to 89.5 percent by weight silica;
(vi) 10 to 25 percent by weight zinc oxide, 0.5 to 50 percent by weight molybdenum oxide, and 25 to 89.5 percent by weight silica;
(vii) 0.5 to 25 percent by weight cerium oxide, 0.5 to 50 percent by weight boron oxide, and 25 to 99 percent by weight silica;
(viii) 0.5 to 25 percent by weight cerium oxide, 0.5 to 50 percent by weight aluminum oxide, and 25 to 99 percent by weight silica;
(ix) 0.5 to 75 percent by weight magnesium or tin oxide, and 25 to 99.5 percent by weight silica;
(x) 0.5 to 25 percent by weight cerium oxide, 0.5 to 25 percent by weight zinc oxide, 0.5 to 25 percent by weight boron oxide, and 25 to 98.5 percent by weight silica;
(xi) 0.5 to 25 percent by weight yttrium oxide, 0.5 to 25 percent by weight phosphorous oxide, 0.5 to 25 percent by weight zinc oxide, and 25 to 98.5 percent by weight silica;
(xii) 0.5 to 5 percent by weight yttrium oxide, 0.5 to 5 percent by weight molybdenum oxide, 0.5 to 25 percent by weight zinc oxide, 0.5 to 5 percent by weight cerium oxide and 60 to 98 percent by weight silica;
and mixtures thereof,
wherein the percent by weights are based on the total weight of the particles.

26. The coating composition of aspect 19, wherein the corrosion resisting particles are prepared by a process comprising:
   (a) introducing a reactant into a plasma chamber;
   (b) heating the reactant by means of a plasma as the reactant flows through the plasma chamber, yielding a gaseous reaction product;
   (c) contacting the gaseous reaction product with a plurality of quench streams injected into the reaction chamber through a plurality of quench gas injection ports, wherein the quench streams are injected at a flow rate and injection angle that results in the impingement of the quench streams with each other within the gaseous reaction product stream, thereby producing ultrafine solid particles; and
   (d) passing the ultrafine solid particles through a converging member.

27. The coating composition of aspect 26, wherein the reactants comprise a solid material.

28. The coating composition of aspect 19, further comprising a film-forming resin.

29. The coating composition of aspect 28, wherein the film-forming resin comprises a polyvinyl polymer.

30. The coating composition of aspect 29, wherein the polyvinyl polymer comprises a polyvinyl butyral resin.

31. The coating composition of aspect 19, wherein the adhesion promoting component comprises phosphatized epoxy resin and/or a free acid selected from tannic acid, gallic acid, phosphoric acid, phosphorous acid, citric acid, malonic acid, a derivative thereof, or a mixture thereof.

32. The coating composition of aspect 19, further comprising conventional non-chrome corrosion resisting pigment particles selected from iron phosphate, zinc phosphate, calcium ion-exchanged silica, colloidal silica, synthetic amorphous silica, and molybdates, such as calcium molybdate, zinc molybdate, barium molybdate, strontium molybdate, or a mixture thereof.

33. The coating composition of aspect 19, further comprising an alkoxysilane and a phenolic resin.

34. A multi-component composite coating comprising at least one coating layer deposited from the coating composition of aspect 19.

35. A metal substrate at least partially coated with the coating composition of aspect 19.

36. A coating composition comprising:
   (a) an adhesion promoting component, and
   (b) corrosion resisting particles having an average primary particle size of no more than 100 nanometers and comprising a plurality of inorganic oxides.

37. The coating composition of aspect 36, wherein at least one inorganic oxide comprises zinc, cerium, yttrium, magnesium, molybdenum, lithium, aluminum, or calcium.

38. A coating composition comprising:
   (1) a film-forming resin, and
   (2) corrosion resisting particles having a calculated equivalent spherical diameter of no more than 200 nanometers and comprising an inorganic oxide,
wherein the corrosion resisting particles are present in the composition in an amount sufficient to result in a composition that, when deposited onto at least a portion of one metal substrate selected from cold rolled steel,
electrogalvanized steel and aluminum and cured, provides a substrate that exhibits corrosion resistance properties greater than the corrosion resistance properties the same substrate exhibits when at least partially coated under the same conditions with a similar coating composition that does not include the corrosion resisting particles.

39. A coating composition that is substantially free of chromium containing material, wherein the coating composition comprises:

1. a film-forming resin, and
2. corrosion resisting particles having a calculated equivalent spherical diameter of no more than 200 nanometers and comprising an inorganic oxide,

wherein the corrosion resisting particles are present in the composition in an amount sufficient to result in a composition that, when deposited onto at least a portion of one metal substrate selected from cold rolled steel, electrogalvanized steel and aluminum and cured, provides a substrate that exhibits corrosion resistance properties at least similar to the corrosion resistance properties that the same substrate exhibits when at least partially coated under the same conditions with a conventional chrome-containing corrosion-resistant composition.

40. A coating composition comprising:

1. a film-forming resin, and
2. corrosion resisting particles selected from (i) particles comprising oxides of cerium, zinc, and silicon; (ii) particles comprising oxides of calcium, zinc and silicon; (iii) particles comprising oxides of phosphorous, zinc and silicon; (iv) particles comprising oxides of yttrium, zinc, and silicon; (v) particles comprising oxides of molybdenum, zinc, and silicon; (vi) particles comprising oxides of boron, zinc, and silicon; (vii) particles comprising oxides of cerium, aluminum, and silicon, (viii) particles comprising oxides of cerium, boron, and silicon, or a mixture thereof.

41. A method for enhancing the corrosion resistance of a metal substrate, comprising coating at least a portion of the substrate with the coating composition of aspect 19.

42. A method of replacing a conventional chrome-containing corrosion-resistant composition, comprising providing the composition of aspect 19.

43. A method for producing ultrafine solid particles, comprising:

(a) introducing a solid precursor into a plasma chamber;
(b) heating the precursor by means of a plasma as the precursor flows through the reaction chamber, yielding a gaseous product stream;
(c) contacting the gaseous product stream with a plurality of quench streams injected into the reaction chamber through a plurality of quench gas injection ports, wherein the quench streams are injected at flow rates and injection angles that result in the impingement of the quench streams with each other within the gaseous product stream, thereby producing ultrafine solid particles; and
(d) passing the ultrafine solid particles through a converging member.

44. An apparatus for producing ultrafine solid particles, comprising:

(a) a plasma chamber having axially spaced inlet and outlet ends;
(b) a plasma positioned at the inlet end of the plasma chamber;
(c) a solid precursor inlet for introducing a solid precursor to the plasma chamber where the precursor is heated by the plasma to produce a gaseous product stream flowing toward the outlet end of the plasma chamber;
(d) a converging member located coaxially within the outlet end of the reactor chamber; and
(e) a plurality of quench gas injection ports located upstream of the converging member, through which a plurality of quench streams are injected into the reaction chamber at flow rates and injection angles that result in the impingement of the quench gas streams with each other at or near the center of the gaseous product stream, thereby producing ultrafine solid particles.
Claims

1. A coating composition comprising
   (1) a film-forming resin, and
   (2) corrosion resisting particles comprising magnesium oxide particles having an average primary particle size
      of no more than 100 nanometers,

2. The coating composition of claim 1 wherein the magnesium oxide particles have an average primary particle size
   of no more than 50 nanometers.

3. The coating composition of claims 1 or 2 wherein the coating composition contains less than 2 weight percent of
   chromium containing material, based on the total weight of the composition.

4. The coating composition of any one of the preceding claims wherein the film-forming resin is a film-forming resin
   for use in automotive OEM coating compositions, automotive refinish coating compositions, industrial coating com-
   positions, architectural coating compositions, coil coating compositions, and aerospace coating compositions.

5. The coating composition of claim 4 wherein the film-forming resin comprises a polyvinyl polymer, preferably a
   polyvinyl butyral resin.

6. The coating composition of any one of the preceding claims wherein the coating composition further comprises an
   adhesion promoting component.

7. The coating composition of claim 6 wherein the adhesion promoting component is selected from free acids, metal
   phosphates, organophosphates, organophosphonates, and a phosphatized epoxy resin.

8. The coating composition of claim 7 wherein the adhesion promoting component is selected from tannic acid, gallic
   acid, phosphoric acid, phosphorous acid, citric acid, malonic acid, or a derivative thereof, or a mixture thereof.

9. The coating composition of any one of claims 6 to 8 wherein the coating composition further comprises a phenolic
   resin and an alkoxysilane.

10. A metal substrate at least partially coated with the coating composition of any one of the preceding claims.

11. A method of at least partially coating a metal substrate comprising applying to the substrate the coating composition
    of any one of claims 1 to 9.

12. The metal substrate or method of claims 10 or 11 wherein the metal substrate is selected from aluminum, aluminum
    alloys, zinc-aluminum alloys and aluminum plated steel.

13. The metal substrate of claim 10 which is an aluminum substrate and wherein the corrosion resisting particles are
    present in the composition in an amount sufficient to result in a composition that, when cured, provides a substrate
    that exhibits corrosion resistance properties greater than the corrosion resistance properties the same substrate
    exhibits when at least partially coated under the same conditions with a similar coating composition that does not
    include the corrosion resisting particles.
REFERENCES CITED IN THE DESCRIPTION

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