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(54) **Title**: REPLENISHING COMPOSITIONS AND METHODS OF REPLENISHING PRETREATMENT COMPOSITIONS

(57) **Abstract**: Disclosed are replenisher compositions and methods of replenishing pretreatment compositions. The methods include adding a replenisher composition to a pretreatment composition wherein the replenisher composition includes (a) a zirconium complex and also optionally includes: (b) a dissolved complex metal fluoride ion wherein the metal ion comprises a Group IIIA metal, Group IVA metal, Group IVB metal, or combinations thereof; (c) a component comprising an oxide, hydroxide, or carbonate of Group IIIA, Group IVA, Group IVB metals; or combinations thereof; and/or (d) a dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof.

REPLENISHING COMPOSITIONS AND METHODS OF REPLENISHING PRETREATMENT COMPOSITIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a continuation-in-part application of application Serial No. 12/575,731, filed October 8, 2009, now U.S. Patent Publication No. 2011/0083580A1, published April 14, 2011.

FIELD OF THE INVENTION

[0002] The present invention relates to replenishing compositions and methods of replenishing pretreatment compositions.

BACKGROUND INFORMATION

[0003] The use of protective coatings on metal surfaces for improved corrosion resistance and paint adhesion characteristics is well known in the metal finishing arts. Conventional techniques involve pretreating metal substrates with phosphate pretreatment coating compositions and chrome-containing rinses for promoting corrosion resistance. The use of such phosphate and/or chromate-containing compositions, however, gives rise to environmental and health concerns. As a result, chromate-free and/or phosphate–free pretreatment compositions have been developed. Such compositions are generally based on chemical mixtures that in some way react with the substrate surface and bind to it to a form protective layer.

[0004] During a typical pretreatment process, as a pretreatment composition is contacted with a substrate, certain ingredients, such as metal ions in the pretreatment composition, bind to the substrate's surface to form a protective layer; as a result the concentration of those ions in the composition may be diminished during the process. Accordingly, it would be desirable to provide a method of replenishing a pretreatment composition with a replenisher composition which replenishes the desired ingredients, such as metal, in the pretreatment composition.

SUMMARY OF THE INVENTION

[0005] In certain respects, the present invention is directed to a method of replenishing a pretreatment composition comprising adding a replenisher composition to the pretreatment composition, wherein the replenisher composition comprises a zirconium complex.

DETAILED DESCRIPTION

[0006] 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.

[0007] 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.

[0008] 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.

[0009] In this application, the use of the singular includes the plural and plural encompasses singular, unless specifically stated otherwise. In addition, in this application, the use of "or" means "and/or" unless specifically stated otherwise, even though "and/or" may be explicitly used in certain instances.

[0010] Unless otherwise indicated, as used herein, "substantially free" means that a composition comprises $\leq$ 1 weight percent, such as $\leq$ 0.8 weight percent or $\leq$ 0.5 weight percent or $\leq$ 0.05 weight percent or $\leq$ 0.005 weight percent, of a particular material (e.g., organic solvent, filler, etc.) based on the total weight of the composition.

[0011] Unless otherwise indicated, as used herein, "completely free" means that a composition does not comprise a particular material (e.g., organic solvent, filler, etc.). That is, the composition comprises 0 weight percent of such material.

[0012] The metal ions and metals referred to herein are those elements included in such designated group of the CAS Periodic Table of the Elements as is shown, for example, in the Handbook of Chemistry and Physics, 68th edition (1987).

[0013] As previously mentioned, certain embodiments of the present invention are directed to methods of replenishing pretreatment compositions comprising adding a replenisher composition to a pretreatment composition. As used herein, the term "replenisher composition" refers to a material added to a pretreatment composition during the pretreatment process. In certain embodiments, the replenisher composition does not have the same formulation as the pretreatment composition although certain components of the formulation may be the same. For example, while both the replenisher composition and the pretreatment composition may both comprise the same material for particular components, respectively, the replenisher composition may comprise components which the pretreatment composition lacks. By way of illustration, the pretreatment composition of the present invention may comprise H_2ZrF_6, while the replenisher composition of the present invention comprises a zirconium complex that may not have been present in the original formulation of the pretreatment composition as well as optionally comprising H_2ZrF_6.

[0014] Moreover, the present invention is not directed to simply adding more pretreatment composition to a pretreatment bath, which comprises the pretreatment composition, in order to replenish the bath. Rather, it is directed to adding a replenisher composition to a pretreatment composition wherein the replenisher composition has a different formulation from that of the pretreatment composition. As stated above, in certain embodiments, the pretreatment composition may include one or more components of a pretreatment bath.

[0015] In certain embodiments, the replenisher composition of certain methods of the present invention comprises (a) a zirconium complex. A zirconium complex, for the purposes of the present invention, is defined as a zirconium compound that is not an oxide, hydroxide, or carbonate of zirconium. Suitable zirconium complex compounds include zirconium compound of a sulfonic acid such as zirconium methanesulphonic acid.

[0016] In certain embodiments, in addition to the zirconium complex (a), the replenisher composition may, optionally, further comprise (b) a dissolved complex metal fluoride ion, wherein the metal ion comprises a Group IIIA metal, Group IVA metal, Group IVB metal, or combinations thereof. The metal can be provided in ionic form, which can be easily dissolved in an aqueous composition at an appropriate pH, as would be recognized by those skilled in the art. The metal may be provided by the addition of specific compounds of the metals, such as their soluble acids and salts. The metal ion of the dissolved complex metal fluoride ion (b) is capable of converting to a metal oxide upon application to a metal substrate. In certain embodiments, the metal ion of dissolved complex metal fluoride ion comprises silicon, germanium, tin, boron, aluminum, gallium, indium, thallium, titanium, zirconium, hafnium, or combinations thereof.

[0017] As mentioned, a source of fluoride ion is also included in the dissolved complex metal fluoride ion (b) to maintain solubility of the metal ions in solution. The fluoride may be added as an acid or as a fluoride salt. Suitable examples include, but are not limited to, ammonium fluoride, ammonium bifluoride, hydrofluoric acid, and the like. In certain embodiments, the dissolved complex metal fluoride ion (b) is provided as a fluoride acid or salt of the metal. In these embodiments, the dissolved complex fluoride ion (b) provides both a metal as well as a source of fluoride to the replenisher composition. Suitable examples include, but are not limited to, fluorosilicic acid, fluorozirconic acid, fluorotitanic acid, ammonium and alkali metal fluorosilicates, fluorozirconates, fluorotitanates, zirconium fluoride, sodium fluoride, sodium bifluoride, potassium fluoride, potassium bifluoride, and the like.

[0018] In certain embodiments, the dissolved complex metal fluoride ion component (b) of the replenisher composition comprises H_2TiF_6, H_2ZrF_6, H_2HfF_6, H_2SiF_6, H_2GeF_6, H_2SnF_6, or combinations thereof.

[0019] In certain embodiments, the dissolved complex metal fluoride ion component (b) of the replenisher composition is present in the replenisher composition in an amount ranging from 1 to 25 percent by weight metal ions, based on the weight of total metal ions of the replenisher composition. In other embodiments, the dissolved complex metal fluoride ion component of the replenisher composition is present in the replenisher composition in an amount ranging from 1 to 15 percent by weight metal ions, such as from 2 to 10 percent by weight metal ions, based on the weight of total metal ions of the replenisher composition.

[0020] In addition to the zirconium complex (a), in certain embodiments with and without the component (b), the replenisher composition may, optionally, further comprise (c) a component comprising an oxide, hydroxide, or carbonate of Group IIIA, Group IVA, Group

IVB metals, or combinations thereof. Suitable examples of Group IIIA, Group IVA, Group IVB metals of component (c) include, but are not limited to, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, titanium, zirconium, hafnium, and the like. In certain embodiments, the metal ion of component (c) comprises titanium, zirconium, hafnium, aluminum, silicon, germanium, tin, or combinations thereof. In other embodiments, component (c) comprises zirconium basic carbonate, aluminum hydroxide, tin oxide, silicon hydroxide, or combinations thereof.

[0021] In still other embodiments, component (c) comprises a zirconyl compound. A zirconyl compound, as defined herein, refers to a chemical compound containing a zirconyl group (ZrO). In certain embodiments, the zirconyl compound in the pretreatment composition comprises zirconyl nitrate ($ZrO(NO_3)_2$), zirconyl acetate ($ZrO(C_2H_3O_2)_2$, zirconyl carbonate ($ZrOCO_3$), protonated zirconium basic carbonate ($Zr_2(OH)_2CO_3$), zirconyl sulfate ($(ZrOSO_4)_2$, zirconyl chloride ($ZrO(Cl)_2$, zirconyl iodide ($ZrO(I)_2$, zirconyl bromide ($ZrO(Br)_2$, or a mixture thereof.

[0022] The replenisher composition of the present invention, in certain of the embodiments, is added to the pretreatment composition to maintain the metal ion content in the pretreatment composition to between 10 ppm ("parts per million") to 250 ppm metal ions (measured as elemental metal), such as from 30 ppm to 200 ppm metal ions, such as from 150 (150) ppm to 200 ppm metal ions in the pretreatment composition. The metal ion content, as defined herein, is the total metal ions contributed from the zirconium complex (a), the optional components (b) and/or (c), when present, in addition to the metal ions in the pretreatment composition not contributed by the replenishing composition.

[0023] Thus, for example, wherein the replenisher composition comprises the zirconium complex (a) without optional components (b) or (c), the total amount of replenisher composition comprising the zirconium complex (a) that is added to the pretreatment composition is such that the total metal ion content in the replenished bath contributed from both the zirconium complex (a) and the remaining metal ions from the pretreatment composition is between 10 ppm ("parts per million") to 250 ppm metal ions (measured as elemental metal), such as from 30 ppm to 200 ppm metal ions, such as from 150 (150) ppm to 200 ppm metal ions in the pretreatment composition. Alternatively, wherein (b) and/or (c) are present, the total amount of replenisher composition added to the pretreatment composition is such that the total metal ion content in the replenished bath contributed from the zirconium complex (a), components (b) and/or (c), and the remaining metal ions from the pretreatment composition is between 10 ppm ("parts per million") to 250 ppm metal ions (measured as elemental metal), such as from 30 ppm to 200 ppm metal ions, such as from 150 (150) ppm to 200 ppm metal ions in the pretreatment composition.

[0024] In certain of these embodiments, the metal ion comprises zirconium. In other embodiments, the metal ion comprises zirconium in combination with another metal ion present in the replenisher composition, as discussed below.

[0025] In certain of these embodiments, wherein both components (b) and (c) are present, at least 8 percent by weight of the metal ions of components (b) and (c) together are provided by the metal ions of component (c). In other embodiments, component (c) is present in the replenisher composition in an amount ranging from 8 to 90 percent by weight metal ions based on the weight of total metal ions of components (b) and (c) of the replenisher composition. In still other embodiments, component (c) is present in the replenisher composition in an amount ranging from 10 to 35 percent by weight metal ions based on the weight of total metal ions of components (b) and (c) of the replenisher composition.

[0026] In certain embodiments, in addition to the zirconium complex (a), in embodiment with our without components (b) and/or (c), the replenisher composition may, optionally, further comprise (d) a dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof.

[0027] In certain embodiments, component (d) comprises manganese, cerium, cobalt, copper, zinc, iron, or combinations thereof. Water-soluble forms of metals can be utilized as a source of the metal ions comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, and/or Lanthanide Series metal. Suitable compounds include, but are not limited to, ferrous phosphate, ferrous nitrate, ferrous sulfate, copper nitrate, copper sulfate, copper chloride, copper sulfamate, zinc nitrate, zinc sulfate, zinc chloride, zinc sulfamate, and the like.

[0028] In certain embodiments, component (d) is present in the replenisher composition at a weight ratio of 1:10 to 10:1 based on the weight of total metal ions of zirconium complex (a) to the weight of total metal ions comprising component (d). In other embodiments, the weight ratio is from 1:6 to 6:1, such as from 1:4 to 4:1 based on the weight of total metal ions of zirconium complex (a) to the weight of total metal ions comprising component (d).

[0029] In certain embodiments, the replenisher composition of the methods of the present invention is provided as an aqueous solution and/or dispersion. In these embodiments, the replenisher composition further comprises water. Water may be used to dilute the replenisher composition used in the methods of the present invention. Any appropriate amount of water may be present in the replenisher composition to provide the desired concentration of other ingredients.

[0030] The pH of the replenisher composition may be adjusted to any desired value. In certain embodiments, the pH of the replenisher composition may be adjusted by varying the amount of the dissolved complex metal fluoride ion present in the composition. In other embodiments, the pH of the replenisher composition may be adjusted using, for example, any acid or base as is necessary. In certain embodiments, the pH of the replenisher is maintained through the inclusion of a basic material, including water soluble and/or water dispersible bases, such as sodium hydroxide, sodium carbonate, potassium hydroxide, ammonium hydroxide, ammonia, and/or amines such as triethylamine, methylethyl amine, or combinations thereof.

[0031] In certain embodiments, the pH of the replenisher may be adjusted by the addition of the zirconium complex (a), particularly by the addition of zirconium methanesulphonic acid, alone or in combination with the optional components (b), (c) and/or (d) described in the previous paragraph.

[0032] In certain embodiments, the replenisher composition, including any of those compositions set forth above, is added to the pretreatment composition in an amount sufficient to maintain the pH of the pretreatment composition at a pH of 6.0 or below. In still other embodiments, the replenisher composition is added to maintain the pH of the pretreatment composition at a level of from 4.0 to 6.0, such as from 4.5 to 5.5.

[0033] In certain embodiments, the replenisher composition of the methods of the present invention is prepared by combining the zirconium complex (a) and water to form a first preblend. The ingredients of the first preblend may be agitated under mild agitation once the ingredients are combined with one another. Next, if component (b), (c) and/or (d) are present, these components (b), (c) and/or (d) and water may be combined to form a second, third and/or fourth preblend, respectively. The ingredients of the second preblend, third and/or fourth preblend may be agitated under mild agitation once the ingredients are combined with one another. The first preblend may then be added to the second, third and/or fourth preblend. Once the first preblends are combined, they may be agitated under mild agitation. The replenisher composition may be prepared at ambient conditions, such as approximately 70°F to 80°F (21 to 26°C), or at temperatures slightly below and/or slightly above ambient conditions, such as from approximately 50°F to 140°F (10 to 60°C).

[0034] In certain embodiments of the methods of the present invention, the replenisher composition may be added to the pretreatment composition under agitation. In other embodiments, the replenisher composition may be added to the pretreatment composition without agitation followed by agitation of the materials. The replenisher composition may be added to the pretreatment composition when the pretreatment composition is at ambient temperature, such as approximately 70°F to 80°F (21 to 26°C), as well as when the pretreatment composition is at temperatures slightly below and/or slightly above ambient temperature, such as, for example, from approximately 50°F to 140°F (10 to 60°C).

[0035] As mentioned, the methods of the present invention are directed toward adding a replenisher composition to a pretreatment composition. As used herein, the term "pretreatment composition" refers to a composition that upon contact with a substrate, reacts with and chemically alters the substrate surface and binds to it to form a protective layer.

[0036] In certain embodiments, the pretreatment composition of the methods of the present invention comprises water and (i) a dissolved complex metal fluoride ion wherein the metal ion comprises a Group IIIA metal, Group IVA metal, Group IVB metal, Group VB metal or combinations thereof.

[0037] The dissolved complex metal fluoride ion (i) of the pretreatment composition may be any of those described above related to the optional dissolved complex metal fluoride ion (b) of the replenisher composition. In certain embodiments, the dissolved complex metal fluoride ion (i) of the pretreatment composition is different from the optional dissolved complex metal fluoride ion (b) of the replenisher composition. In other embodiments, the dissolved complex metal fluoride ion (i) of the pretreatment composition is the same as the optional dissolved complex metal fluoride ion (b) of the replenisher composition.

[0038] In certain embodiments, the metal ion of the optional dissolved complex metal fluoride ion (b) of the pretreatment composition comprises titanium, zirconium, hafnium, silicon, germanium, tin, or combinations thereof. In certain embodiments, the dissolved complex metal fluoride ion of component (i) of the pretreatment composition comprises H_2TiF_6, H_2ZrF_6, H_2HfF_6, H_2SiF_6, H_2GeF_6, H_2SnF_6, or combinations thereof.

[0039] In certain embodiments, the dissolved complex metal fluoride ion (i) is present in the pretreatment composition in an amount to provide a concentration of from 10 ppm ("parts per million") to 250 ppm metal ions (measured as elemental metal), such as from 30 ppm to 200 ppm metal ions, such as from 150 ppm to 200 ppm metal ions in the pretreatment composition.

[0040] In certain embodiments, the pretreatment composition may, optionally, further comprise (ii) a dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof. The dissolved metal ion (ii) of the pretreatment composition, if used, may be any of those described above related to the optional dissolved metal ion (d) of the replenisher composition. In certain embodiments, the dissolved metal ion (ii) of the pretreatment composition is different from the optional dissolved metal ion (d) of the replenisher composition. In other embodiments, the dissolved metal ion (ii) of the pretreatment composition is the same as the optional dissolved metal ion (d) of the replenisher composition.

[0041] In some embodiments, if the pretreatment composition comprises the dissolved metal ion of component (ii), then the replenisher composition will comprise the optional dissolved metal ion of component (d). Alternatively, in some embodiments, if the pretreatment composition does not comprise the dissolved metal ion of component (ii), then the replenisher composition may or may not comprise the optional dissolved metal ion of component (d).

[0042] In certain embodiments, the dissolved metal ion (ii) of the pretreatment composition comprises manganese, cerium, cobalt, copper, zinc, or combinations thereof. Suitable compounds include, but are not limited to, ferrous phosphate, ferrous nitrate, ferrous sulfate, copper nitrate, copper sulfate, copper chloride, copper sulfamate, zinc nitrate, zinc sulfate, zinc chloride, zinc sulfamate, and the like.

[0043] In certain embodiments, the dissolved metal ion (ii) is present in the pretreatment composition in an amount to provide a concentration of from 5 ppm to 200 ppm metal ions (measured as elemental metal), such as from 10 ppm to 100 ppm metal ions in the pretreatment composition.

[0044] As mentioned, the pretreatment composition also comprises water. Water may be present in the pretreatment composition at any appropriate amount to provide the desired concentration of other ingredients.

[0045] In certain embodiments, the pretreatment composition comprises materials which are present to adjust pH. In certain embodiments, the pH of the pretreatment composition ranges from 2.0 to 7.0, such as from 3.5 to 6.0. The pH of the pretreatment composition described here relates to the pH of the composition prior to contacting the pretreatment composition with a substrate during the pretreatment process. The pH of the pretreatment composition may be adjusted using, for example, any acid or base as is necessary. In certain embodiments, the pH of the pretreatment composition is maintained through inclusion of a basic material, including water soluble and/or water dispersible bases, such as sodium hydroxide, sodium carbonate, potassium hydroxide, ammonium hydroxide, ammonia, and/or amines such as triethylamine, methylethyl amine, or combinations thereof

[0046] The pretreatment composition may optionally contain other materials, including but not limited to nonionic surfactants, water dispersible organic solvents, defoamers, wetting agents, fillers, and resinous binders.

[0047] Suitable water dispersible organic solvents and their amounts are described in U.S. Patent Application Pub. No. 2009/0032144A1, paragraph [0039], the cited portion being incorporated herein by reference. In other embodiments, the pretreatment composition is substantially free or, in some cases, completely free of any water dispersible organic solvents.

[0048] Suitable resinous binders, as well as their weight percents, which may be used in connection with the pretreatment composition disclosed herein are described in U.S. Patent Application Pub. No. 2009/0032144A1, paragraph [0036] through paragraph [0038], the cited portion being incorporated herein by reference.

[0049] Suitable fillers that may be used in connection with the pretreatment composition disclosed herein are described in U.S. Patent Application Pub. No. 2009/0032144A1, paragraph [0042], the cited portion being incorporated herein by reference. In other embodiments, the pretreatment composition is substantially free or, in some cases, completely free of any filler.

[0050] In certain embodiments, the pretreatment composition also comprises a reaction accelerator, such as nitrite ions, nitrate ions, nitro-group containing compounds, hydroxylamine sulfate, persulfate ions, sulfite ions, hyposulfite ions, peroxides, iron (III) ions, citric acid iron compounds, bromate ions, perchlorate ions, chlorate ions, chlorite ions as well as ascorbic acid, citric acid, tartaric acid, malonic acid, succinic acid and salts thereof. Specific examples of such materials, as well as their amounts in the pretreatment composition, are described in U.S. Patent Application Pub. No. 2009/0032144A1 at paragraph [0041] and in U.S. Patent Application Pub. No. 2004/0163736, paragraph [0032] through paragraph [0041], the cited portions being incorporated herein by reference. In other embodiments, the pretreatment composition is substantially free or, in some cases, completely free of a reaction accelerator.

[0051] In certain embodiments, the pretreatment composition also comprises phosphate ions. Suitable materials and their amounts are described in U.S. Patent Application Pub. No. 2009/0032144A1 at paragraph [0043], incorporated herein by reference. In certain embodiments, however, the pretreatment composition is substantially or, in some cases, completely free of phosphate ion. As used herein, the term "substantially free" when used in reference to the absence of phosphate ion in the pretreatment composition, means that phosphate ion is present in the composition in an amount less than 10 ppm. As used herein, the term "completely free", when used with reference to the absence of phosphate ions, means that there are no phosphate ions in the composition at all.

[0052] In certain embodiments, the pretreatment composition is substantially or, in some cases, completely free of chromate and/or heavy metal phosphate, such as zinc phosphate.

[0053] As would be recognized in the art, parameters of a pretreatment composition other than concentration of metal ions as described above may be monitored during the pretreatment process, including for example pH and concentration of reaction products. As used herein, the term "reaction products" refers to soluble and/or insoluble substances that are formed during deposition of a pretreatment composition onto a substrate and from materials added to the pretreatment composition to control bath parameters, including the replenisher composition, and does not include the pretreatment film formed on the substrate. If any of these parameters fall outside of a desired concentration range, the effectiveness of depositing a metal compound onto a substrate can be impacted. For example, the pH of the pretreatment composition may decrease over time (e.g., become too acidic) which can impact the effectiveness of depositing metal compound onto the substrate.

[0054] Similarly, an increased concentration of reaction products present in a pretreatment composition can also interfere with proper formation of the pretreatment coating onto a substrate which can lead to poor properties, including corrosion resistance. For example, in some cases, as a metal compound is deposited onto a substrate's surface, fluoride ions associated with the metal compound can become dissociated from the metal compound and released into the pretreatment composition as free fluoride, and if left unchecked, will increase with time. As used herein, "free fluoride" refers to isolated fluoride ions that are no longer complexed and/or chemically associated with a metal ion and/or hydrogen ion, but rather independently exist in the bath. As used herein, "total fluoride" refers to the combined amount of free fluoride and fluoride that is complexed and/or chemically associated with a metal ion and/or hydrogen ion, i.e., fluoride which is not free fluoride. As will be appreciated by those skilled in the art, any suitable method for determining the concentration of free fluoride and total fluoride may be used, including for example, ion selective electrode analysis (ISE) using a calibrated meter capable of such measurements, such as an Accumet XR15 meter with an Orion Ionplus Sure-Flow Fluoride Combination electrode (available from Fisher Scientific).

[0055] In certain embodiments, the initial concentration of free fluoride of the pretreatment composition ranges from 10 to 200 ppm. In other embodiments, the initial concentration of free fluoride of the pretreatment composition ranges from 20 to 150 ppm.

[0056] In certain embodiments, a pH controller may be added to the pretreatment composition in addition to the replenisher composition to achieve a desired pH. Any suitable pH controller commonly known in the art may be used, including for example, any acid or base as is necessary. Suitable acids include, but are not limited to, sulfuric acid and nitric acid. Suitable water soluble and/or water dispersible bases include, but are not limited to, sodium hydroxide, sodium carbonate, potassium hydroxide, ammonium hydroxide, ammonia, and/or amines such as triethylamine, methylethyl amine, or combinations thereof. In certain embodiments, a pH controller may be added to the pretreatment composition during the pretreatment process to adjust the pH of the pretreatment composition to a pH of 6.0 or below, such as a pH of 5.5 or below, such as a pH of 5.0 or below. In other embodiments, the pH controller may be added to adjust the pH to a level of from 4.0 to 5.0, such as from 4.6 to 4.8.

[0057] In certain embodiments, the addition of the replenisher composition may maintain the pH of the pretreatment composition thereby reducing and/or eliminating the amount of pH controller that is added during the pretreatment process. In certain embodiments, addition of the replenisher composition results in addition of a pH controller at a lesser frequency during the pretreatment process. That is, addition of a pH controller to the pretreatment composition occurs a lesser number of times, compared to methods other than the present invention. In other embodiments, addition of the replenisher composition results in a lesser amount of a pH controller that is added to the pretreatment composition during the pretreatment process compared to the amount of a pH controller that is added according to methods other than the methods of the present invention.

[0058] In certain embodiments, the level of reaction product may be controlled through an overflow method, as would be recognized by those skilled in the art, in addition to the addition of the replenisher composition. In other embodiments, a reaction product scavenger may be added to the pretreatment composition in addition to the replenisher composition. As used herein, a "reaction product scavenger" refers to a material that, when added to a pretreatment composition during the pretreatment process, complexes with reaction products, for example free fluoride, present in the pretreatment composition, to remove the reaction products from the composition. Any suitable reaction product scavenger commonly known in the art may be used. Suitable reaction product scavengers include, but are not limited to, those described in U.S. Patent Application Pub. No. 2009/0032144A1, paragraphs [0032] through [0034], incorporated herein by reference.

[0059] In certain embodiments, the addition of the replenisher composition may result in lower concentrations of reaction products during the pretreatment process thereby reducing and/or eliminating the amount of a reaction product scavenger that is added to a pretreatment composition during the pretreatment process. In some embodiments, it is believed that because the concentration of reaction products is lower as a result of addition of the replenisher composition, the level of sludge which may build during the pretreatment process is reduced and/or eliminated, although the inventors do not wish to be bound by any particular theory.

[0060] In certain embodiments, addition of the replenisher composition results in addition of a reaction product scavenger at a lesser frequency during the pretreatment process. That is, addition of a reaction product scavenger to the pretreatment composition occurs a lesser number of times, compared to methods other than the methods of the present invention. In other embodiments, addition of the replenisher composition results in a lesser amount of a reaction product scavenger that is added to the pretreatment composition during the pretreatment process compared to the amount of a reaction product scavenger that is added according to methods other than the methods of the present invention.

[0061] In certain embodiments, the present invention is directed toward a method of replenishing a pretreatment composition comprising: (I) adding a replenisher composition to the pretreatment composition, wherein the replenisher composition comprises (a) a zirconium complex and may, optionally, further comprise one or more of (b) a dissolved complex metal fluoride ion wherein the metal ion comprises a Group IIIA metal, Group IVA metal, Group IVB metal, or combinations thereof; (c) a component comprising an oxide, hydroxide, or carbonate of Group IIIA, Group IVA, Group IVB metals or combinations thereof; and (d) a dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof; and wherein the pretreatment composition comprises: (i) a dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof; (ii) a dissolved complex metal fluoride ion wherein the metal atom comprises a Group IIIA metal, Group IVA metal, Group IVB metal, Group VB metal, or combinations thereof; and water; and (II) agitating the blend of replenisher composition and pretreatment composition.

[0062] In certain embodiments, the present invention is directed toward a method of replenishing a pretreatment composition comprising: (I) adding a replenisher composition to the pretreatment composition, wherein the replenisher composition comprises a) a zirconium complex and may, optionally, further comprise one or more of (b) a dissolved complex metal fluoride ion wherein the metal ion comprises a Group IIIA metal, Group IVA metal, Group IVB metal, or combinations thereof; (c) a component comprising an oxide, hydroxide, or carbonate of Group IIIA, Group IVA, Group IVB metals or combinations thereof; and (d) a dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof; and wherein the pretreatment composition comprises: (i) a dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal; a Lanthanide Series metal, or combinations thereof; and water; and (II) agitating the blend of replenisher composition and pretreatment composition.

[0063] In certain embodiments, the pretreatment composition replenished by the replenisher composition according to the methods of the present invention may be applied to a metal substrate. Suitable metal substrates for use in the present invention include those that are often used in the assembly of automotive bodies, automotive parts, and other articles, such as small metal parts, including fasteners, i.e., nuts, bolts, screws, pins, nails, clips, buttons, and the like. Specific examples of suitable metal substrates include, but are not limited to, cold rolled steel, hot rolled steel, steel coated with zinc metal, zinc compounds, or zinc alloys, such as electrogalvanized steel, hot-dipped galvanized steel, galvannealed steel, and steel plated with zinc alloy. Also, aluminum alloys, aluminum plated steel and aluminum alloy plated steel substrates may be used. Other suitable non-ferrous metals include copper and magnesium, as well as alloys of these materials. Moreover, the metal substrate may be a cut edge of a substrate that is otherwise treated and/or coated over the rest of its surface. The metal substrate may be in the form of, for example, a sheet of metal or a fabricated part.

[0064] The substrate may first be cleaned to remove grease, dirt, or other extraneous matter. This is often done by employing mild or strong alkaline cleaners, such as are commercially available and conventionally used in metal pretreatment processes. Examples of alkaline cleaners suitable for use in the present invention include CHEMKLEEN 163, CHEMKLEEN 177, and CHEMKLEEN 490MX, each of which are commercially available from PPG Industries, Inc. Such cleaners are often followed and/or preceded by a water rinse.

[0065] In certain embodiments, the pretreatment composition replenished according to the methods of the present invention may be brought into contact with the substrate by any of known techniques, such as dipping or immersion, spraying, intermittent spraying, dipping followed by spraying, spraying followed by dipping, brushing, or roll-coating. In certain embodiments, the pretreatment composition when applied to the metal substrate is at a temperature ranging from 50 to 150°F (10 to 65°C). The contact time is often from 10 seconds to five minutes, such as 30 seconds to 2 minutes.

[0066] In certain embodiments, the applied metal ion of the pretreatment coating composition generally ranges from 1 to 1000 milligrams per square meter (mg/m^2), such as 10 to 400 mg/m^2. The thickness of the pretreatment coating can vary, but it is generally very thin, often having a thickness of less than 1 micrometer, in some cases it is from 1 to 500 nanometers, and, in yet other cases, it is 10 to 300 nanometers.

[0067] Following contact with the pretreatment solution, the substrate may be rinsed with water and dried.

[0068] In certain embodiments, after the substrate is contacted with the pretreatment composition which has been replenished according to the methods of the present invention, it is then contacted with a coating composition comprising a film-forming resin. Any suitable technique may be used to contact the substrate with such a coating composition, including, for example, brushing, dipping, flow coating, spraying and the like. In certain embodiments, such contacting comprises an electrocoating step wherein an electrodepositable composition is deposited onto the metal substrate by electrodeposition.

[0069] As used herein, the term "film-forming resin" refers to resins that can form a self-supporting continuous film on at least a horizontal surface of a substrate upon removal of any diluents or carriers present in the composition or upon curing at ambient or elevated temperature. Conventional film-forming resins that may be used include, without limitation, those typically used in automotive OEM coating compositions, automotive refinish coating compositions, industrial coating compositions, architectural coating compositions, coil coating compositions, and aerospace coating compositions, among others.

[0070] In certain embodiments, the coating composition comprises a thermosetting film-forming resin. As used herein, the term "thermosetting" refers to resins that "set" irreversibly upon curing or crosslinking, wherein the polymer chains of the polymeric components are joined together by covalent bonds. This property is usually associated with a cross-linking reaction of the composition constituents often induced, for example, by heat or radiation. Curing or crosslinking reactions also may be carried out under ambient conditions. Once cured or crosslinked, a thermosetting resin will not melt upon the application of heat and is insoluble in solvents. In other embodiments, the coating composition comprises a thermoplastic film-forming resin. As used herein, the term "thermoplastic" refers to resins that comprise polymeric components that are not joined by covalent bonds and thereby can undergo liquid flow upon heating and are soluble in solvents.

[0071] As previously mentioned, the substrate may be contacted with a coating composition comprising a film-forming resin by an electrocoating step wherein an electrodepositable coating is deposited onto the metal substrate by electrodeposition. Suitable electrodepositable coating compositions include those described in U.S. Patent Application Pub. No. 2009/0032144A1, paragraph [0051] through paragraph [0082], the cited portion of which being incorporated herein by reference.

[0072] Illustrating the invention are the following examples that are not to be considered as limiting the invention to their details. All parts and percentages in the examples, as well as throughout the specification, are by weight unless otherwise indicated.

EXAMPLES

Example 1

[0073] A replenisher composition was prepared as follows. The amount of each of the ingredients present in the replenisher composition of Example 1 is reflected in Table 1 below. Each of the percentages is expressed by weight.

TABLE 1

Hexafluorozirconic acid, 45% (available from Honeywell)	5.6%
Zirconium basic carbonate (available from Blue Line Corporation)	1.3%
Copper nitrate solution, 18% copper (available from Shepherd Chemical)	1.8%
Deionized water	balance

[0074] The following materials were used:

- CHEMFIL BUFFER, alkaline buffer solution commercially available from PPG Industries, Inc.
- CHEMKLEEN 166HP, alkaline cleaning product commercially available from PPG Industries, Inc.
- CHEMKLEEN 171A, alkaline cleaning product commercially available from PPG Industries, Inc.
- ZIRCOBOND CONTROL #4, commercially available from PPG Industries, Inc.
- ZIRCOBOND R1, replenisher commercially available from PPG Industries, Inc.

[0075] A fresh zirconium pretreatment bath was prepared using 0.88 grams per liter of hexafluorozirconic acid (45%) and 1.08 grams per liter of a copper nitrate solution (concentration 2% copper by weight). The remainder of the bath was deionized water. The pH of the bath was adjusted to approximately 4.5 with CHEMFIL BUFFER.

[0076] Two 3.7 liter aliquots of the above pretreatment bath were tested as follows, one with ZIRCOBOND R1 and the other with the replenisher composition of Example 1. To test each of the replenishers, panels were pretreated in 3.7 liters of the pretreatment bath previously described to deplete it, and then each bath was adjusted using the appropriate replenisher.

[0077] The initial levels of zirconium and free fluoride were measured in each bath. The level of zirconium was measured by x-rite fluorescence. The initial zirconium level of the bath to be replenished with ZIRCOBOND R1 was approximately 187 ppm (measured as elemental metal). The initial zirconium level of the bath to be replenished with the replenisher composition of Example 1 was approximately 183 ppm (measured as elemental metal).

[0078] The initial free fluoride of each of the baths was measured by ion selective electrode (ISE) analysis using a calibrated Accumet XR15 meter with an Orion Ionplus Sure-Flow Fluoride Combination electrode (model # 960900) (available from Fisher Scientific) using the following method. The meter was calibrated using fluoride calibration standards mixed with a buffer which were prepared as follows: fifty (50) milliliters of 10% trisodium citrate buffer solution was added to each two (2) milliliter sample of 100 mg/L, 300 mg/L and 1,000 mg/L fluoride standard. To measure free fluoride, a neat sample to be analyzed (i.e., without buffer) was added to a clean beaker, and the Accumet XR15 meter probe was placed into the sample. Once the reading stabilized, the value was recorded. This value was divided by twenty-six (26) to arrive at the concentration of free fluoride. The initial free fluoride of the baths was approximately 21 to 22 ppm.

[0079] Panels were prepared for processing through the baths as follows. The panels were cleaned for two (2) minutes by spray application in a 2% v/v solution of CHEMKLEEN 166HP with 0.2% CHEMKLEEN 171A added. The panels were rinsed by immersing for approximately ten (10) seconds into deionized water, followed by an approximately ten (10) second spray with deionized water.

[0080] A group of twenty (20) 4 x 6” panels were processed through each bath, the selection of panels consisted of: one (1) panel of aluminum (6111 T43); one (1) panel of cold rolled steel; two (2) hot dipped galvanized steel panels; and sixteen (16) electrogalvanized steel panels. The panels were immersed into the pretreatment bath for two (2) minutes at approximately 80°F (28°C), with mild agitation. Next, the panels were rinsed with an approximately 10 – 15 second spray with deionized water, and dried with a warm air blow-off.

[0081] After processing the first group of 20 panels through the bath, each of the pretreatment baths was measured for zirconium level, pH, and fluoride level using the methods described above.

[0082] Based on these measurements, ZIRCOBOND R1 and the replenisher composition of Example 1 was added to each respective bath to adjust the zirconium level of the bath back to the starting value. Adjustments to bring the pH within the range of 4.4 - 4.8 and free fluoride level within the range of from 40-70 ppm were also made, if any adjustment was necessary. The pH was adjusted (if necessary) by adding CHEMFIL BUFFER to each of the baths. Free fluoride was adjusted (if necessary) by adding ZIRCOBOND CONTROL #4 to each of the baths.

[0083] The bath depletion and replenishment process described above was continued in 20 panel groupings until a total of 300 panels had been treated in each bath. The amounts of ZIRCOBOND R1 and replenisher composition of Example 1, CHEMFIL BUFFER, and ZIRCOBOND CONTROL #4 added to each of the baths were recorded. Any sludge that formed in the baths was also collected and measured. The results are shown in Table 2 below:

TABLE 2

Replenisher Composition	Bath Chemical Usage (grams)			Sludge generated (grams)
	Replenisher	Chemfil Buffer	Zircobond Control #4	
ZIRCOBOND R1	54.3 g	7.4 g	8.7 g	1.6 g
Example 1	48.9 g	3.4 g	3.1 g	0.9 g

Example 2

[0084] A replenisher composition was prepared as follows. The amount of each of the ingredients present in the replenisher composition of Example 1 is reflected in Table 1 below. Each of the percentages is expressed by weight. The amount of methanesulfonic acid present is enough to give a stoichiometric ratio of 4:1 to the zirconium provided by the zirconium basic carbonate.

TABLE 3

Hexafluorozirconic acid, 45% (available from Honeywell)	17.58%
Zirconium basic carbonate (available from Blue Line Corporation)	5.86%
Methanesulfonic acid (available from Sigma-Aldrich Company)	7.42%
Copper nitrate solution, 18% copper (available from Shepherd Chemical)	7.6%
Deionized water	balance

[0085] In addition to the above-mentioned materials used in Example 1, the following materials were used:

- ZIRCOBOND ZRF, a zirconium pretreatment make-up product commercially available from PPG Industries, Inc.
- CHEMKLEEN 2010LP, alkaline cleaning product commercially available from PPG Industries, Inc.
- CHEMKLEEN 181ALP, alkaline cleaning product commercially available from PPG Industries, Inc.

[0086] A fresh zirconium pretreatment bath was prepared using 10.04 grams per liter of ZIRCOBOND ZRF in deionized water. The pH of the bath was adjusted to approximately 4.5 with CHEMFIL BUFFER.

[0087] A four liter aliquot of the pretreatment bath was tested as follows: Panels were pretreated in the pretreatment bath to deplete it, as in Example 1, and then the bath was adjusted using the replenisher described in Table 2.

[0088] The initial levels of zirconium and free fluoride were measured in the bath as described in Example 1. The level of zirconium was measured at 186 ppm (measured as elemental metal. The initial free fluoride was measured at 128 ppm.

[0089] Panels were prepared for processing through the bath in a similar fashion to Example 1, as follows. The panels were cleaned for two (2) minutes by spray application in a 1.25% v/v solution of CHEMKLEEN 2010LP with 0.125% CHEMKLEEN 181ALP added. The panels were rinsed by immersing for approximately ten (10) seconds into deionized water, followed by an approximately ten (10) second spray with deionized water.

[0090] A group of panels was then processed through the bath. The group consisted of the following: eight 4" x 12" hot dipped galvanized panels; two 4" x 6" hot dipped galvanized panels; one 4” x 6” panel of aluminum (6111 T43); and one 4” x 6” panel of cold rolled steel. The amount of surface area in this group was identical to the panel groups from Example 1; the ratio of zin-coated (galvanized) to cold rolled steel to aluminum was also the same, except that in this Example the galvanized metal consisted entirely of hot dipped galvanized panels. The panels were immersed into the pretreatment bath for two (2) minutes at approximately 73°F (23°C), with mild agitation. Next, the panels were rinsed with an approximately 10 – 15 second spray with deionized water, and dried with a warm air blow-off.

[0091] After processing the first group of 20 panels through the bath, each of the pretreatment baths was measured for zirconium level, pH, and fluoride level using the methods previously described.

[0092] Based on these measurements, the replenisher composition of Example 2 was added to the bath to adjust the zirconium level of the bath back to the starting value. Adjustments to bring the pH within the range of 4.5 - 4.8 and free fluoride level within the range of from 100-160 ppm were also made, if any adjustment was necessary. The pH was adjusted (if necessary) by adding CHEMFIL BUFFER to the bath. Free fluoride was adjusted (if necessary) by adding ZIRCOBOND CONTROL #4 to the bath.

[0093] The bath depletion and replenishment process described above was continued in the described panel grouping until a surface area equivalent to 320 4” x 6” panels or 160 4” x 12” panels (i.e., 16 groups of panels) had been treated in the bath. The amounts of replenisher composition of Example 2, CHEMFIL BUFFER, and ZIRCOBOND CONTROL #4 added to the bath was recorded. The results are shown in Table 4 below:

TABLE 4

Replenisher Composition	Bath Chemical Usage (grams)		
	Replenisher	Chemfil Buffer	Zircobond Control #4
Example 2	17.92 g	2.2 g	4.81 g

[0094] The amount of chemical necessary to remove excess free fluoride and maintain the free fluoride at the starting level was thus significantly less than the ZIRCOBOND R1 as described in Example 1, even though the amount of metal treated was slightly higher.

[0095] Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

WE CLAIM:

1. A method of replenishing a pretreatment composition comprising:

adding a replenisher composition to the pretreatment composition, wherein the replenisher composition comprises a zirconium complex.

2. The method of Claim 1, wherein the zirconium complex comprises zirconium methanesulphonic acid.

3. The method of claim 1, wherein the replenisher composition further comprises a dissolved complex metal fluoride ion wherein the metal ion comprises a Group IIIA metal, Group IVA metal, Group IVB metal, or combinations thereof.

4. The method of Claim 3, wherein the dissolved complex metal fluoride ion of the replenisher composition comprises H_2TiF_6, H_2ZrF_6, H_2HfF_6, H_2SiF_6, H_2GeF_6, H_2SnF_6, or combinations thereof.

5. The method of Claim 3, wherein the metal of the dissolved complex metal fluoride ion comprises titanium, zirconium, hafnium, aluminum, silicon, germanium, tin, or combinations thereof.

6. The method of claim 1, wherein the replenisher composition further comprises a component comprising an oxide, hydroxide, carbonate of Group IIIA metals, Group IVA metals, Group IVB metals, or combinations thereof.

7. The method of Claim 6, wherein the component comprising an oxide, hydroxide, carbonate of Group IIIA metals, Group IVA metals, Group IVB metals, or combinations thereof comprises a zirconyl compound.

8. The method of Claim 7, wherein the zirconyl compound comprises zirconyl nitrate, zirconyl acetate, zirconyl carbonate, protonated zirconium basic carbonate, zirconyl sulfate, zirconyl chloride, zirconyl iodide, zirconyl bromide, or combinations thereof.

9. The method of claim 1, wherein the replenisher composition further comprises:

a dissolved complex metal fluoride ion wherein the metal ion comprises a Group IIIA metal, Group IVA metal, Group IVB metal, or combinations thereof; and

a component comprising an oxide, hydroxide, carbonate of Group IIIA metals, Group IVA metals, Group IVB metals, or combinations thereof.

10. The method of Claim 1, wherein the replenisher composition further comprises:

a dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof.

11. The method of Claim 10, wherein the dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof comprises manganese, cerium, cobalt, copper, zinc, or combinations thereof.

12. The method of Claim 6, wherein the replenisher composition further comprises:

a dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof

13. The method of Claim 12, wherein the dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof comprises manganese, cerium, cobalt, copper, zinc, or combinations thereof.

14. The method of Claim 1, wherien the replenisher composition is added to the pretreatment composition in an amount sufficient to maintain the total metal ion content of the pretreatment composition to between 10 ppm and 250 ppm.

15. The method of Claim 9, wherein the replenisher composition further comprises:

a dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof.

16. The method of Claim 15, wherein the dissolved metal ion comprising a Group IB metal, Group IIB metal, Group VIIB metal, Group VIII metal, Lanthanide Series metal, or combinations thereof comprises manganese, cerium, cobalt, copper, zinc, or combinations thereof.

17. The method of Claim 1 further comprising agitating the replenisher composition and pretreatment composition

18. A replenished pretreatment composition according to Claim 1

19. A method for treating a substrate comprising contacting the substrate with the replenished pretreatment composition of Claim 18.

20. A treated substrate formed in accordance with the method of Claim 19.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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C23C

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/044099 A1 (PPG IND OHIO INC [US]; CHENG SHAN [US]; DECHANT JAMES A [US]; FOTINOS) 14 April 2011 (2011-04-14) the whole document -----	1,3-8, 10-14, 17-20
X	WO 2009/117397 A1 (HENKEL CORP [DE]; GOODREAU BRUCE H [US]; LIU JIANPING [US]; KAPIC EDIS) 24 September 2009 (2009-09-24) page 13, paragraph 50 - page 14, paragraph 51 page 18, paragraph 71-72; examples G, I, II; table 1a page 19, line 21; examples Formula 1, 2, 7, 8 ----- -/--	1,3-8, 10-14, 17-20

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

☒ See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

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(54) 发明名称

补充组合物和补充预处理组合物的方法

(57) 摘要

公开的是补充剂组合物和补充预处理组合物的方法。该方法包括将补充剂组合物加入到预处理组合物中，其中该补充剂组合物包括 (a) 锆络合物，以及还任选的包括：(b) 溶解的络合物金属氟化物离子，其中该金属离子包含 IIIA 族金属，IVA 族金属，IVB 族金属或者其组合；(c) 组分，其包含 IIIA 族，IVA 族，IVB 族金属的氧化物、氢氧化物或者碳酸盐；或者其组合；和/或 (d) 溶解的金属离子，其包含 IB 族金属，IIB 族金属，VIIB 族金属，VIII 族金属，镧系金属或者其组合。

CN 104145045 A

1. 一种补充预处理组合物的方法，其包含：

将补充剂组合物加入该预处理组合物中，其中该补充剂组合物包含锆络合物。

2. 权利要求1的方法，其中该锆络合物包括锆甲烷磺酸。

3. 权利要求1的方法，其中该补充剂组合物进一步包含溶解的络合物金属氟化物离子，其中该金属离子包括IIIA族金属、IVA族金属、IVB族金属或者其组合。

4. 权利要求3的方法，其中该补充剂组合物的溶解的络合物金属氟化物离子包括H_2TiF_6、H_2ZrF_6、H_2HfF_6、H_2SiF_6、H_2GeF_6、H_2SnF_6或者其组合。

5. 权利要求3的方法，其中该溶解的络合物金属氟化物离子的金属包括钛、锆、铪、铝、硅、锗、锡或者其组合。

6. 权利要求1的方法，其中该补充剂组合物进一步包含这样的组分，该组分包含IIIA族金属、IVA族金属、IVB族金属的氧化物、氢氧化物、碳酸盐或者其组合。

7. 权利要求6的方法，其中该包含IIIA族金属、IVA族金属、IVB族金属的氧化物、氢氧化物、碳酸盐或者其组合的组分包括氧锆基化合物。

8. 权利要求7的方法，其中该氧锆基化合物包括硝酸氧锆、乙酸氧锆、碳酸氧锆、质子化的碱式碳酸锆、硫酸氧锆、氯化氧锆、碘化氧锆、溴化氧锆或者其组合。

9. 权利要求1的方法，其中该补充剂组合物进一步包含：

溶解的络合物金属氟化物离子，其中该金属离子包括IIIA族金属、IVA族金属、IVB族金属或者其组合；和

包含IIIA族金属、IVA族金属、IVB族金属的氧化物、氢氧化物、碳酸盐或者其组合的组分。

10. 权利要求1的方法，其中该补充剂组合物进一步包含：

溶解的金属离子，其包含IB族金属、IIB族金属、VIIB族金属、VIII族金属、镧系金属或者其组合。

11. 权利要求10的方法，其中该包含IB族金属、IIB族金属、VIIB族金属、VIII族金属、镧系金属或者其组合的溶解的金属离子包括锰、铈、钴、铜、锌或者其组合。

12. 权利要求6的方法，其中该补充剂组合物进一步包含：

溶解的金属离子，其包含IB族金属、IIB族金属、VIIB族金属、VIII族金属、镧系金属或者其组合。

13. 权利要求12的方法，其中该包含IB族金属、IIB族金属、VIIB族金属、VIII族金属、镧系金属或者其组合的溶解的金属离子包括锰、铈、钴、铜、锌或者其组合。

14. 权利要求1的方法，其中将该补充剂组合物以这样的量加入预处理组合物中，该量足以将预处理组合物的总金属离子含量保持到10ppm-250ppm。

15. 权利要求9的方法，其中该补充剂组合物进一步包含：

溶解的金属离子，其包含IB族金属、IIB族金属、VIIB族金属、VIII族金属、镧系金属或者其组合。

16. 权利要求15的方法，其中该包含IB族金属、IIB族金属、VIIB族金属、VIII族金属、镧系金属或者其组合的溶解的金属离子包括锰、铈、钴、铜、锌或者其组合。

17. 权利要求1的方法，其进一步包括搅拌该补充剂组合物和预处理组合物。

18. 根据权利要求1补充的预处理组合物。

19. 一种处理基材的方法，其包括将该基材与权利要求 18 的补充的预处理组合物接触。

20. 一种处理的基材，其是根据权利要求 19 的方法形成的。

补充组合物和补充预处理组合物的方法

[0001] 交叉参考的相关申请

[0002] 本申请是 2009 年 10 月 8 日提交的申请系列 No. 12/575731（现在的 2011 年 4 月 14 日公开的美国专利公开 No. 2011/0083580A1）的部分继续申请。

发明领域

[0003] 本发明涉及补充组合物和补充预处理组合物的方法。

[0004] 背景信息

[0005] 在金属表面上使用保护性涂层来改进耐腐蚀性和油漆附着特性是金属整饰领域公知的。常规的技术包括用磷酸盐预处理涂料组合物预处理金属基材和含铬冲洗来促进耐腐蚀性。但是，使用这样的磷酸盐和／或含铬酸盐的组合物导致了环境和健康问题。结果，已经开发了无铬酸盐和／或无磷酸盐的预处理组合物。这样的组合物通常基于化学混合物，其以某些方式与基材表面反应和结合到它上来形成保护层。

[0006] 在典型的预处理方法过程中，当预处理组合物与基材接触时，某些成分例如预处理组合物中的金属离子结合到基材表面上来形成保护性层；结果，组合物中那些离子的浓度会在所述方法过程中减少。因此，令人期望的是提供一种用补充剂组合物补充预处理组合物的方法，其补充了预处理组合物中期望的成分例如金属。

发明内容

[0007] 在某些方面，本发明涉及一种补充预处理组合物的方法，其包含将补充剂组合物加入该预处理组合物中，其中该补充剂组合物包含锆络合物。

具体实施方式

[0008] 在下面的具体实施方式中，应当理解本发明可以赋予不同的可选择的变化和步骤次序，除了有明确的相反规定之处。此外，除了任何操作实施例或者另有指示之处外，表示例如说明书和权利要求中所用的成分的量的全部数字被理解为在全部的情况中是用术语“约”修正的。因此，除非有相反的指示，否则下面的说明书和附加的权利要求中阐明的数字参数是近似的，其可以根据本发明所寻求获得的期望的性能而变化。最起码，和并非打算使用等价原则来限制权利要求的范围，每个数字参数应当至少按照所报告的有效数字的数值和通过使用通常的四舍五入技术来解释。

[0009] 虽然阐明本发明宽的范围的数字范围和参数是近似的，但是在具体实施例中所述的数值是尽可能精确来报告的。但是任何数值本质上包含了由它们各自的测试测量中存在的标准偏差所必然形成的某些误差。

[0010] 同样，应当理解这里所述的任何数字范围目的是包括处于其中的全部的子范围。例如范围“1-10”目的是包括在所述的最小值 1 和所述的最大值 10 之间（并包括其）的全部子范围，即，具有最小值等于或者大于 1 和最大值等于或者小于 10。

[0011] 在本申请中，单数的使用包括复数和包含单数的复数，除非另有明确规定。另外，

在本申请中，使用“或者”表示“和／或”，除非另有明确规定，即使在某些情况中可以明确使用“和／或”。

[0012] 作为此处使用的，除非另有指示，否则“基本不含”表示组合物包含≤ 1 重量％，例如≤ 0.8 重量％或者≤ 0.5 重量％或者≤ 0.05 重量％或者≤ 0.005 重量％的具体材料（例如有机溶剂，填料等），基于该组合物的总重量。

[0013] 作为此处使用的，除非另有指示，“完全不含”表示组合物不包含具体的材料（例如有机溶剂，填料等）。即，该组合物包含 0 重量％的这样的材料。

[0014] 在此提及的金属离子和金属是包括在 CAS 元素周期表的这样指定的族中的那些元素，如 Handbook of Chemistry and Physics，第 68 版 (1987) 中所示。

[0015] 如前所述，本发明的某些实施方案涉及补充预处理组合物的方法，其包含将补充剂组合物加入预处理组合物中。作为此处使用的，术语“补充剂组合物”指的是在预处理方法期间加入到预处理组合物中的材料。在某些实施方案中，该补充剂组合物具有与预处理组合物不同的配方，虽然该配方的某些组分可以相同。例如，虽然该补充剂组合物和预处理组合物二者都可以分别包含用于具体组分的相同的材料，但是该补充剂组合物可以包含预处理组合物所缺少的组分。举例说明，本发明的预处理组合物可以包含 H_2ZrF_6，而本发明的补充剂组合物包含锆络合物（其可以不存在于预处理组合物的初始配方中）以及任选的包含 H_2ZrF_6。

[0016] 此外，本发明不涉及简单的加入更多的预处理组合物到预处理浴（其包含预处理组合物）来补充该浴。而是，它涉及到将补充剂组合物加入预处理组合物中，其中该补充剂组合物具有与预处理组合物不同的配方。如上所述，在某些实施方案中，该预处理组合物可以包括预处理浴的一种或多种组分。

[0017] 在某些实施方案中，本发明某些方法的补充剂组合物包含 (a) 锆络合物。在本发明中，锆络合物定义为锆化合物，其不是锆的氧化物、氢氧化物或者碳酸盐。合适的锆络合物化合物包括磺酸的锆化合物例如锆甲烷磺酸。

[0018] 在某些实施方案中，除了锆络合物 (a) 之外，该补充剂组合物可以任选的进一步包含 (b) 溶解的络合物金属氟化物离子，其中该金属离子包含 IIIA 族金属，IVA 族金属，IVB 族金属或者其组合。该金属可以以离子形式提供，其会在适当的 pH 时易溶于含水组合物中，如本领域技术人员公认的那样。该金属可以通过加入金属具体的化合物来提供，例如它们的可溶性酸和盐。该溶解的络合物金属氟化物离子 (b) 的金属离子能够在施用到金属基材时转化成金属氧化物。在某些实施方案中，该溶解的络合物金属氟化物离子的金属离子包含硅，锗，锡，硼，铝，镓，铟，铊，钛，锆，铪或者其组合。

[0019] 如所述的，氟离子源也包括在该溶解的络合物金属氟化物离子 (b) 中，来保持该金属离子在溶液中的溶解度。该氟化物可以作为酸或者作为氟化物盐加入。合适的例子包括但不限于氟化铵，氟化氢铵，氢氟酸等。在某些实施方案中，该溶解的络合物金属氟化物离子 (b) 是作为金属的氟化物酸或者盐来提供的。在这些实施方案中，该溶解的络合物氟离子 (b) 将金属以及氟化物源二者提供给该补充剂组合物。合适的例子包括但不限于氟硅酸，氟锆酸，氟钛酸，铵和碱金属氟硅酸盐，氟锆酸盐，氟钛酸盐，氟化锆，氟化钠，氟化氢钠，氟化钾，氟化氢钾等。

[0020] 在某些实施方案中，该补充剂组合物的溶解的络合物金属氟化物离子组分 (b) 包

含 H_2TiF_6，H_2ZrF_6，H_2HfF_6，H_2SiF_6，H_2GeF_6，H_2SnF_6 或其组合。

[0021] 在某些实施方案中，该补充剂组合物的溶解的络合物金属氟化物离子组分 (b) 是以 1-25 重量％金属离子的量存在于该补充剂组合物中，基于该补充剂组合物的总金属离子重量。在其他实施方案中，该补充剂组合物的溶解的络合物金属氟化物离子组分是以 1-15 重量％的金属离子，例如 2-10 重量％的金属离子的量存在于该补充剂组合物中，基于该补充剂组合物的总金属离子的重量。

[0022] 除了锆络合物 (a) 之外，在具有或者不具有组分 (b) 的某些实施方案中，该补充剂组合物可以任选的进一步包含 (c) 组分，其包含 IIIA 族，IVA 族，IVB 族金属的氧化物、氢氧化物或者碳酸盐，或者其组合。组分 (c) 的 IIIA 族，IVA 族，IVB 族金属合适的例子包括但不限于铝，镓，铟，铊，硅，锗，锡，铅，钛，锆，铪等。在某些实施方案中，组分 (c) 的金属离子包含钛，锆，铪，铝，硅，锗，锡或其组合。在其他实施方案中，组分 (c) 包含碱式碳酸锆，氢氧化铝，氧化锡，氢氧化硅或者其组合。

[0023] 在仍然的其他实施方案中，组分 (c) 包含氧锆基化合物。作为这里定义的，氧锆基化合物指的是含有氧锆基 (ZrO) 的化学化合物。在某些实施方案中，预处理组合物中的氧锆基化合物包含硝酸氧锆 ($ZrO(NO_3)_2$)，乙酸氧锆 ($ZrO(C_2H_3O_2)_2$，碳酸氧锆 ($ZrOCO_3$)，质子化的碱式碳酸锆 ($Zr_2(OH)_2CO_3$)，硫酸氧锆 ($ZrOSO_4)_2$，氯化氧锆 ($ZrO(Cl)_2$，碘化氧锆 ($ZrO(I)_2$，溴化氧锆 ($ZrO(Br)_2$ 或者其混合物。

[0024] 本发明的补充剂组合物在某些实施方案中被加入到预处理组合物中，来将预处理组合物中的金属离子含量保持在 10ppm(“份／百万”)-250ppm 金属离子 (作为元素金属来测量)，例如预处理组合物中 30ppm-200ppm 金属离子，例如 150(150)ppm-200ppm 金属离子。作为这里定义的，该金属离子含量是总金属离子，其除了预处理组合物中非来自补充组合物的金属离子之外，还来自于锆络合物 (a)，在存在时的任选的组分 (b) 和／或 (c)。

[0025] 因此，例如其中补充剂组合物包含锆络合物 (a)，而没有任选的组分 (b) 或 (c) 时，加入到预处理组合物中的包含锆络合物 (a) 的补充剂组合物的总量是这样，即，补充的浴中来自于锆络合物 (a) 和预处理组合物的其余金属离子二者的总金属离子含量是 10ppm(“份／百万”)-250ppm 金属离子 (作为元素金属)，例如预处理组合物中 30ppm-200ppm 金属离子，例如 150(150)ppm-200ppm 金属离子。可选择的，在其中存在 (b) 和／或 (c) 时，加入到预处理组合物中的补充剂组合物的总量是这样，即，补充浴中来自于锆络合物 (a)，组分 (b) 和／或 (c) 和预处理组合物中的其余金属离子的总金属离子含量是 10ppm(“份／百万”)-250ppm 金属离子 (作为元素金属)，例如预处理组合物中 30ppm-200ppm 金属离子，例如 150(150)ppm-200ppm 金属离子。

[0026] 在这些实施方案的某些中，该金属离子包含锆。在其他实施方案中，该金属离子包含锆和相组合的存在于该补充剂组合物中的另一种金属离子，如下所述。

[0027] 在这些实施方案的某些中，在其中存在着组分 (b) 和 (c) 二者，组分 (b) 和 (c) 一起的至少 8 重量％的金属离子是通过组分 (c) 的金属离子提供的。在其他实施方案中，组分 (c) 在补充剂组合物中的存在量是 8-90 重量％的金属离子，基于补充剂组合物的组分 (b) 和 (c) 的总金属离子重量。在仍然的其他实施方案中，组分 (c) 在该补充剂组合物中的存在量是 10-35 重量％的金属离子，基于补充剂组合物的组分 (b) 和 (c) 的总金属离子重量。

[0028] 在某些实施方案中，除了锆络合物 (a) 之外，在具有或不具有组分 (b) 和／或 (c)

的实施方案中，该补充剂组合物可以任选的进一步包含 (d) 溶解的金属离子，其包含 IB 族金属，IIB 族金属，VIIB 族金属，VIII 族金属，镧系金属或其组合。

[0029] 在某些实施方案中，组分 (d) 包含锰，铈，钴，铜，锌，铁或其组合。水溶性形式的金属可以用作包含 IB 族金属，IIB 族金属，VIIB 族金属，VIII 族金属和 / 或镧系金属的金属离子的源。合适的化合物包括但不限于磷酸亚铁，硝酸亚铁，硫酸亚铁，硝酸铜，硫酸铜，氯化铜，氨基磺酸铜，硝酸锌，硫酸锌，氯化锌，氨基磺酸锌等。

[0030] 在某些实施方案中，组分 (d) 在补充剂组合物中是以 1 :10-10 :1 的重量比存在的，基于锆络合物 (a) 的总金属离子重量与组分 (d) 所包含的总金属离子的重量。在其他实施方案中，该重量比是 1 :6-6 :1，例如 1 :4-4 :1，基于锆络合物 (a) 的总金属离子重量与组分 (d) 所包含的总金属离子的重量。

[0031] 在某些实施方案中，本发明方法的补充剂组合物是作为水溶液和 / 或分散体来提供的。在这些实施方案中，该补充剂组合物进一步包含水。水可以用于稀释本发明方法所用的补充剂组合物。任何适量的水可以存在于该补充剂组合物中，来提供期望浓度的其他成分。

[0032] 该补充剂组合物的 pH 可以调整为任何期望的值。在某些实施方案中，该补充剂组合物的 pH 可以通过改变组合物是所存在的溶解的络合物金属氟化物离子的量来改变。在其他实施方案中，该补充剂组合物的 pH 可以使用例如任何所需的酸或碱来调整。在某些实施方案中，该补充剂的 pH 是通过包含碱性材料来保持的，包括水可溶性和 / 或水可分散性碱，例如氢氧化钠，碳酸钠，氢氧化钾，氢氧化铵，氨和 / 或胺例如三乙胺，甲基乙基胺或者其组合。

[0033] 在某些实施方案中，该补充剂的 pH 可以通过加入锆络合物 (a)，特别是通过加入锆甲烷磺酸来调整，其单独加入或者与前段所述的任选的组分 (b)，(c) 和 / 或 (d) 相组合来加入。

[0034] 在某些实施方案中，该补充剂组合物，包括上述任何的那些组合物，是以这样的量加入到预处理组合物中的，该量足以将预处理组合物的 pH 保持在 pH 为 6.0 或以下。在仍然的其他实施方案中，将该补充剂组合物加入来将预处理组合物的 pH 保持在 4.0-6.0，例如 4.5-5.5 的水平。

[0035] 在某些实施方案中，本发明方法的补充剂组合物是通过将锆络合物 (a) 和水合并来形成第一预混物来制备的。一旦所述成分彼此合并之后，该第一预混物的成分可以在适度搅拌下进行搅拌。接着，如果存在组分 (b)，(c) 和 / 或 (d)，则这些组分 (b)，(c) 和 / 或 (d) 和水可以合并来分别形成第二、第三和 / 或第四预混物。一旦所述成分彼此合并之后，该第二预混物，第三和 / 或第四预混物的成分可以在适度搅拌下进行搅拌。第一预混物然后可以加入到第二，第三和 / 或第四预混物中。一旦第一预混物合并，则它们可以在适度搅拌下搅拌。该补充剂组合物可以在环境条件下制备，例如约 70 -80 (21-26℃)，或者在稍低于和 / 或稍高于环境条件的温度，例如约 50 -140 (10-60℃)。

[0036] 在本发明方法的某些实施方案中，该补充剂组合物可以在搅拌下加入预处理组合物中。在其他实施方案中，该补充剂组合物可以不搅拌加入预处理组合物中，随后搅拌所述材料。当预处理组合物处于环境温度例如约 70 -80 (21-26℃)，以及当预处理组合物处于稍低于和 / 或稍高于环境温度例如诸如约 50 -140 (10-60℃) 的温度时，该补充剂组

合物可以加入到预处理组合物中。

[0037] 如所述的，本发明的方法涉及将补充剂组合物加入预处理组合物中。作为此处使用的，术语“预处理组合物”指的是这样的组合物，其通过与基材接触，而与基材表面反应和化学改变该基材表面和结合到其上来形成保护层。

[0038] 在某些实施方案中，本发明方法的预处理组合物包含水和 (i) 溶解的络合物金属氟化物离子，其中该金属离子包含 IIIA 族金属，IVA 族金属，IVB 族金属，基团 VB 金属或者其组合。

[0039] 该预处理组合物的溶解的络合物金属氟化物离子 (i) 可以是任何上述的那些，其涉及到该补充剂组合物的任选的溶解的络合物金属氟化物离子 (b)。在某些实施方案中，该预处理组合物的溶解的络合物金属氟化物离子 (i) 不同于该补充剂组合物的任选的溶解的络合物金属氟化物离子 (b)。在其他实施方案中，该预处理组合物的溶解的络合物金属氟化物离子 (i) 与该补充剂组合物的任选的溶解的络合物金属氟化物离子 (b) 相同。

[0040] 在某些实施方案中，该预处理组合物的任选的溶解的络合物金属氟化物离子 (b) 的金属离子包含钛，锆，铪，硅，锗，锡或其组合。在某些实施方案中，该预处理组合物的组分 (i) 的溶解的络合物金属氟化物离子包含 H_2TiF_6，H_2ZrF_6，H_2HfF_6，H_2SiF_6，H_2GeF_6，H_2SnF_6 或者其组合。

[0041] 在某些实施方案中，该溶解的络合物金属氟化物离子 (i) 在该预处理组合物中以一定量存在，来提供 10ppm(“份 / 百万”)-250ppm 金属离子 (作为元素金属来测量) 的浓度，例如在预处理组合物中 30ppm-200ppm 的金属离子，例如 150ppm-200ppm 的金属离子。

[0042] 在某些实施方案中，该预处理组合物可以任选的进一步包含 (ii) 溶解的金属离子，其包含 IB 族金属，IIB 族金属，VIIB 族金属，VIII 族金属，镧系金属或者其组合。如果使用，该预处理组合物的溶解的金属离子 (ii) 可以是任何上述的那些，其涉及该补充剂组合物的任选的溶解的金属离子 (d)。在某些实施方案中，该预处理组合物的溶解的金属离子 (ii) 不同于该补充剂组合物的任选的溶解的金属离子 (d)。在其他实施方案中，该预处理组合物的溶解的金属离子 (ii) 与该补充剂组合物的任选的溶解的金属离子 (d) 相同。

[0043] 在一些实施方案中，如果该预处理组合物包含组分 (ii) 的溶解的金属离子，则该补充剂组合物将包含组分 (d) 的任选的溶解的金属离子。可选择的，在一些实施方案中，如果该预处理组合物不含组分 (ii) 的溶解的金属离子，则该补充剂组合物可以或者可以不包含组分 (d) 的任选的溶解的金属离子。

[0044] 在某些实施方案中，该预处理组合物的溶解的金属离子 (ii) 包含锰，铈，钴，铜，锌或者其组合。合适的化合物包括但不限于磷酸亚铁，硝酸亚铁，硫酸亚铁，硝酸铜，硫酸铜，氯化铜，氨基磺酸铜，硝酸锌，硫酸锌，氯化锌，氨基磺酸锌等。

[0045] 在某些实施方案中，该溶解的金属离子 (ii) 在预处理组合物中以一定量存在，来提供 5ppm-200ppm 金属离子 (作为元素金属测量) 的浓度，例如在预处理组合物中 10ppm-100ppm 的金属离子。

[0046] 如所述的，该预处理组合物也包含水。水在预处理组合物中可以以任何适当的量存在，来提供其他成分期望的浓度。

[0047] 在某些实施方案中，该预处理组合物包含用于调整 pH 而存在的材料。在某些实施方案中，预处理组合物的 pH 是 2.0-7.0，例如 3.5-6.0。这里所述的预处理组合物的 pH 涉

及到在预处理方法过程中，预处理组合物与基材接触之前该组合物的 pH。预处理组合物的 pH 可以使用例如所需的任何酸或碱来调整。在某些实施方案中，该预处理组合物的 pH 是通过包含碱性材料来保持的，包括水可溶性和 / 或水可分散性碱，例如氢氧化钠，碳酸钠，氢氧化钾，氢氧化铵，氨和 / 或胺例如三乙胺，甲基乙基胺或者其组合。

[0048] 该预处理组合物可以任选的包含其他材料，包括但不限于非离子表面活性剂，水可分散性有机溶剂，消泡剂，润湿剂，填料和树脂质粘合剂。

[0049] 合适的水可分散性有机溶剂和它们的量描述在美国专利申请公开 No. 2009/0032144A1 第 [0039] 段中，该引用部分在此引入作为参考。在其他实施方案中，该预处理组合物基本不含或者在一些情况中完全不含任何的水可分散性有机溶剂。

[0050] 合适的树脂质粘合剂以及它们的重量百分比（其可以与这里公开的预处理组合物一起使用）描述在美国专利申请公开 No. 2009/0032144A1 第 [0036] 段到 [0038] 段中，该引用部分在此引入作为参考。

[0051] 可以与这里公开的预处理组合物一起使用的合适的填料描述在美国专利申请公开 No. 2009/0032144A1 第 [0042] 段中，该引用部分在此引入作为参考。在其他实施方案中，该预处理组合物基本不含或者在一些情况中完全不含任何的填料。

[0052] 在某些实施方案中，该预处理组合物还包含反应加速剂，例如亚硝酸盐离子，硝酸盐离子，含硝基的化合物，羟基胺硫酸盐，过硫酸盐离子，亚硫酸盐离子，次硫酸盐离子，过氧化物，铁（III）离子，柠檬酸铁化合物，溴酸盐离子，高氯酸盐离子，氯酸盐离子，亚氯酸盐离子以及抗坏血酸，柠檬酸，酒石酸，丙二酸，琥珀酸及其盐。这样的材料具体的例子以及它们在预处理组合物中的量描述在美国专利申请公开 No. 2009/0032144A1 的第 [0041] 段和美国专利申请公开 No. 2004/0163736 第 [0032] 段到 [0041] 段，该引用部分在此引入作为参考。在其他实施方案中，该预处理组合物基本不含或者在一些情况中完全不含任何的反应加速剂。

[0053] 在某些实施方案中，该预处理组合物还包含磷酸盐离子。合适的材料和它们的量描述在美国专利申请公开 No. 2009/0032144A1 的第 [0043] 段，在此引入作为参考。但是在某些实施方案中，该预处理组合物基本不含或者在一些情况中完全不含磷酸盐离子。作为此处使用的，术语“基本不含”当用于表示预处理组合物中不存在磷酸盐离子，这意味着磷酸盐离子在该组合物中的存在量小于 10ppm。作为此处使用的，术语“完全不含”当用于表示不存在磷酸盐离子时，这意味着该组合物中根本不存在磷酸盐离子。

[0054] 在某些实施方案中，该预处理组合物基本不含或者在一些情况中完全不含铬酸盐和 / 或重金属磷酸盐，例如磷酸锌。

[0055] 作为本领域公知的，除了上述的金属离子浓度之外，在预处理方法中可以监控预处理组合物的参数，包括例如 pH 和反应产物的浓度。作为此处使用的，术语“反应产物”指的是可溶性和 / 或不可溶性物质，其是在预处理组合物沉积到基材上的过程中形成的，并且来自于加入到预处理组合物中来控制浴参数的材料，其包括该补充剂组合物，并且不包括在基材上所形成的预处理膜。如果任何的这些参数落入期望的浓度范围之外，则会影响金属化合物在基材上沉积的有效性。例如预处理组合物的 pH 会随时间而降低（例如变成过强酸性的），这会影响金属化合物在基材上沉积的有效性。

[0056] 类似的，预处理组合物中存在的反应产物浓度的增加也会干扰基材上预处理涂层

的正确形成，这会导致差的性能，包括耐腐蚀性。例如在一些情况中，当金属化合物沉积到基材表面上时，与金属化合物有关的氟离子会变得与该金属化合物分离和作为游离氟离子释放到预处理组合物中，并且如果置之不理，则将随时间而增加。作为此处使用的，“游离氟离子”指的是分离的氟离子，其不再与金属离子和／或氢离子络合和／或化学相连，而是独立存在于所述浴中。作为此处使用的，“总氟离子”指的是游离氟离子和与金属离子和／或氢离子络合和／或化学相连的氟离子（即，非游离氟离子的氟离子）的合计量。作为本领域技术人员所理解的，可以使用任何用于测定游离氟离子和总氟离子浓度的合适的方法，包括例如离子选择性电极分析 (ISE)，其使用能够进行这样的测量的校正计，例如 Accumet XR15 计，其具有 Orion Ionplus Sure-Flow Fluoride 组合电极（获自 Fisher Scientific）。

[0057] 在某些实施方案中，预处理组合物的游离氟离子的初始浓度是 10-200ppm。在其他实施方案中，预处理组合物的游离氟离子的初始浓度是 20-150ppm。

[0058] 在某些实施方案中，除了补充剂组合物之外，pH 控制剂可以加入到该预处理组合物中，来实现期望的 pH。可以使用本领域公知的任何合适的 pH 控制剂，包括例如所需的任何酸或碱。合适的酸包括但不限于硫酸和硝酸。合适的水溶性和／或水分散性碱包括但不限于氢氧化钠，碳酸钠，氢氧化钾，氢氧化铵，氨和／或胺例如三乙胺，甲乙胺或者其组合。在某些实施方案中，pH 控制剂可以在预处理方法期间加入该预处理组合物中，来将预处理组合物的 pH 调整为 pH 为 6.0 或以下，例如 pH 为 5.5 或以下，例如 pH 为 5.0 或以下。在其他实施方案中，pH 控制剂可以加入来将 pH 调整到 4.0-5.0，例如 4.6-4.8 的水平。

[0059] 在某些实施方案中，加入该补充剂组合物可以保持预处理组合物的 pH，由此减少和／或消除在预处理方法期间所加入的 pH 控制剂的量。在某些实施方案中，加入该补充剂组合物导致了在预处理方法期间 pH 控制剂的加入频率较低。即，与非本发明的方法相比，将 pH 控制剂加入到预处理组合物中是以较少次数来进行的。在其他实施方案中，加入该补充剂组合物导致了与非本发明方法的方法中所加入的 pH 控制剂的量相比，在该预处理方法期间加入到预处理组合物中的 pH 控制剂的量较小。

[0060] 在某些实施方案中，除了加入该补充剂组合物之外，反应产物的水平可以通过溢流方法来控制，如本领域技术人员公知的那样。在其他实施方案中，除了补充剂组合物之外，反应产物猝灭剂可以加入到该预处理组合物中。作为此处使用的，“反应产物猝灭剂”指的是这样的材料，其当在预处理方法期间加入到预处理组合物中时，与预处理组合物中存在的反应产物例如游离氟离子络合，来从组合物中除去反应产物。可以使用本领域公知的任何合适的反应产物猝灭剂。合适的反应产物猝灭剂包括但不限于描述在美国专利申请公开 No. 2009/0032144A1 第 [0032]-[0034] 段中的那些，其在此引入作为参考。

[0061] 在某些实施方案中，加入该补充剂组合物会导致预处理方法期间反应产物浓度降低，由此减少和／或消除在预处理方法期间加入到预处理组合物中的反应产物猝灭剂的量。在一些实施方案中，据信因为反应产物的浓度由于补充剂组合物的加入而是较低的，因此减少和／或消除了在预处理方法期间所积聚的淤浆的水平，虽然本发明人不希望受限于任何具体的理论。

[0062] 在某些实施方案中，加入该补充剂组合物导致了在预处理方法期间反应产物猝灭剂的加入频率较低。即，与非本发明方法的方法相比，将反应产物猝灭剂加入到预处理组合物中是以较少次数来进行的。在其他实施方案中，加入该补充剂组合物导致了与非本发明

方法的方法中所加入的反应产物猝灭剂的量相比，在该预处理方法期间加入到预处理组合物中的反应产物猝灭剂的量较小。

[0063] 在某些实施方案中，本发明涉及一种补充预处理组合物的方法，其包含：(I) 将补充剂组合物加入该预处理组合物中，其中该补充剂组合物包含 (a) 锆络合物，并且可以任选的进一步包含一种或多种的 (b) 溶解的络合物金属氟化物离子，其中该金属离子包含 IIIA 族金属，IVA 族金属，IVB 族金属或其组合；(c) 组分，其包含 IIIA 族，IVA 族，IVB 族金属的氧化物、氢氧化物或者碳酸盐或其组合；和 (d) 溶解的金属离子，其包含 IB 族金属，IIB 族金属，VIIB 族金属，VIII 族金属，镧系金属或其组合；和其中该预处理组合物包含：(i) 溶解的金属离子，其包含 IB 族金属，IIB 族金属，VIIB 族金属，VIII 族金属，镧系金属或者其组合；(ii) 溶解的络合物金属氟化物离子，其中该金属原子包含 IIIA 族金属，IVA 族金属，IVB 族金属，第 VB 族金属或其组合；和水；和 (II) 搅拌该补充剂组合物和预处理组合物的混合物。

[0064] 在某些实施方案中，本发明涉及一种补充预处理组合物的方法，其包含：(I) 将补充剂组合物加入预处理组合物中，其中该补充剂组合物包含 a) 锆络合物，并且可以任选的进一步包含一种或多种的 (b) 溶解的络合物金属氟化物离子，其中该金属离子包含 IIIA 族金属，IVA 族金属，IVB 族金属或其组合；(c) 组分，其包含 IIIA 族，IVA 族，IVB 族金属的氧化物、氢氧化物或者碳酸盐或其组合；和 (d) 溶解的金属离子，其包含 IB 族金属，IIB 族金属，VIIB 族金属，VIII 族金属，镧系金属或其组合；和其中该预处理组合物包含：(i) 溶解的金属离子，其包含 IB 族金属，IIB 族金属，VIIB 族金属，VIII 族金属；镧系金属或其组合；和水；和 (II) 搅拌该补充剂组合物和预处理组合物的混合物。

[0065] 在某些实施方案中，将根据本发明的方法，用补充剂组合物补充的预处理组合物可以施用到金属基材上。用于本发明的合适的金属基材包括那些，其经常用于车体的组件，汽车零件，和其他制品，例如小金属零件，其包括紧固件，即，螺母，螺栓，螺杆，销子，钉子，夹子，按钮等。合适的金属基材的例子包括但不限于冷轧钢，热轧钢，用锌金属、锌化合物或者锌合金涂覆的钢，例如电镀锌钢，热浸镀锌钢，镀锌钢，和锌合金电镀的钢。同样可以使用铝合金，镀铝钢和铝合金电镀的钢基材。其他合适的非铁金属包括铜和镁，以及这些材料的合金。此外，该金属基材可以是基材的切割边缘，其是在它的其余表面上处理和／或涂覆的。该金属基材可以处于例如金属片或者制作的零件的形式。

[0066] 该基材可以首先清洁来除去油脂、脏物或者其他异物。这通常是使用中等或者强碱性清洁剂来进行的，例如是市售的和通常用于金属预处理方法的。适用于本发明的碱性清洁剂的例子包括 CHEMKLEEN163，CHEMKLEEN177 和 CHEMKLEEN490MX，其每个市售自 PPG Industries，Inc。这样的清洁剂经常在水冲洗之后和／或之前。

[0067] 在某些实施方案中，根据本发明的方法补充的预处理组合物可以通过任何已知的技术来与基材接触，例如浸涂或者浸没，喷涂，间歇喷涂，浸涂随后喷涂，喷涂随后浸涂，刷涂或者辊涂。在某些实施方案中，该预处理组合物当施涂到金属基材上时处于 50-150 ℉（10-65℃）的温度。接触时间经常是 10 秒 -5 分钟，例如 30 秒 -2 分钟。

[0068] 在某些实施方案中，预处理涂料组合物所施涂的金属离子通常是 1-1000 毫克／平方米 (mg/m^2)，例如 10-400mg/m^2。该预处理涂层的厚度可以变化，但是它通常非常薄，经常具有小于 1 微米的厚度，在一些情况中它是 1-500 纳米，和在仍然的其他情况中，它是

10-300 纳米。

[0069] 在与预处理溶液接触后，该基材可以用水冲洗和干燥。

[0070] 在某些实施方案中，在基材与预处理组合物（其已经根据本发明的方法进行了补充）接触之后，它然后与包含成膜树脂的涂料组合物接触。任何合适的技术可以用于将基材与这样的涂料组合物接触，包括例如刷涂，浸涂，流涂，喷涂等。在某些实施方案中，这样的接触包含电涂步骤，其中将可电沉积组合物通过电沉积沉积到金属基材上。

[0071] 作为此处使用的，术语"成膜树脂"指的是这样的树脂，其可以通过除去组合物中存在的任何稀释剂或载体或者通过在环境温度或高温固化，来在基材的至少水平表面上形成自持性连续膜。可以使用的常规成膜树脂包括但不限于典型的用于汽车 OEM 涂料组合物，汽车整修涂料组合物，工业涂料组合物，建筑涂料组合物，线圈涂料组合物和航天涂料组合物等的那些。

[0072] 在某些实施方案中，该涂料组合物包含热固性成膜树脂。作为这里使用的，术语"热固性"指的是这样的树脂，其通过固化或者交联而不可逆的"固着"，其中该聚合物组分的聚合物链通过共价键连接在一起。这种性能通常与例如经常由于热或辐射诱导的组合物的成分的交联反应有关。固化或交联反应也可以在环境条件下进行。一旦固化或交联，则热固性树脂将在施加热时不熔融和不溶于溶剂。在其他实施方案中，该涂料组合物包含热塑性成膜树脂。作为此处使用的，术语"热塑性"指的是树脂包含不通过共价键连接的聚合物组分和由此可以在加热时发生液体流动和可溶于溶剂中。

[0073] 如前所述，该基材与包含成膜树脂的涂料组合物通过电涂步骤接触，其中通过电沉积将可电沉积的涂料沉积到金属基材上。合适的可电沉积涂料组合物包括描述在美国专利申请公开 No. 2009/0032144A1 第 [0051]-[0082] 段的那些，其的引用部分在此引入作为参考。

[0074] 说明本发明的是下面的实施例，其不被认为是将本发明限制到它们的细节。实施例以及整个说明书中全部的份数和百分比是重量的，除非另有指示。

[0075] 实施例

[0076] 实施例 1

[0077] 补充剂组合物是如下来制备的。实施例 1 的补充剂组合物中存在的每个成分的量反映在下表 1 中。每个百分比是用重量表达的。

[0078] 表 1

[0079]

六氟锆酸，45%（获自 Honeywell）	5.6%
碱式碳酸锆（获自 Blue Line Corporation）	1.3%
硝酸铜溶液，18%铜（获自 Shepherd Chemical）	1.8%
去离子水	余量

[0080] 使用下面的材料：

[0081] CHEMFIL BUFFER，碱性缓冲液溶液，市售自 PPG Industries, Inc.

[0082] CHEMKLEEN 166HP，碱性清洁产品，市售自 PPG Industries, Inc.

[0083] CHEMKLEEN 171A,碱性清洁产品,市售自 PPG Industries,Inc.

[0084] ZIRCOBOND 对照 #4,市售自 PPG Industries,Inc.

[0085] ZIRCOBOND R1,补充剂,市售自 PPG Industries,Inc.

[0086] 一种新的锆预处理浴是使用 0.88g/L 六氟锆酸(45%)和 1.08g/L 硝酸铜溶液(浓度 2 重量%铜)来制备的。该浴液的其余部分是去离子水。用 CHEMFIL BUFFER 将该浴液的 pH 调整到约 4.5。

[0087] 如下来测试了上述预处理浴液的两个 3.7 升等分部分,一个用 ZIRCOBOND R1 和另一个用实施例 1 的补充剂组合物。为了测试每个补充剂,将面板在 3.7 升的前述预处理浴中预处理来贫化它,然后将每个浴使用适当的补充剂进行调整。

[0088] 测量了每个浴液中锆和游离氟离子的初始水平。锆的水平是通过 x-rite 荧光测量的。打算用 ZIRCOBOND R1 补充的浴液中的初始锆水平是约 187ppm(作为元素金属来测量)。打算用实施例 1 的补充剂组合物补充的浴液中初始锆水平是约 183ppm(作为元素金属来测量)。

[0089] 每个浴液的初始游离氟离子是通过离子选择性电极(ISE)分析,使用具有 Orion Ionplus Sure-Flow Fluoride 组合电极的校准的 Accumet XR15 计(型号 #960900)(获自 Fisher Scientific),使用下面的方法来测量的。该仪器是使用混合有缓冲液的氟离子校准标准物来校正的,其是如下来制备的:将五十(50)毫升的 10%柠檬酸三钠缓冲液溶液加入到 100mg/L,300mg/L 和 1000mg/L 氟离子标准物的每个二(2)毫升样品中。为了测量游离氟离子,将待分析的纯净样品(即,没有缓冲液)加入到洁净烧杯中,和将 Accumet XR15 计探针置于该样品中。一旦读数稳定后,记录所述值。将这个值除以二十六(26)来达到游离氟离子的浓度。所述浴液的初始游离氟离子是约 21-22ppm。

[0090] 制备了面板,用于穿过浴液如下来加工。通过在 CHEMKLEEN166HP 的 2% v/v 溶液中用所加入的 0.2%的 CHEMKLEEN171A 喷涂来将所述面板清洁二(2)分钟。将该面板浸入去离子水中约十(10)秒,随后用去离子水喷涂约十(10)秒来冲洗。

[0091] 将一组二十(20)个 4x6”面板穿过每个浴液来加工,面板的选择组成为:一个(1)面板是铝(6111T43);一个(1)面板是冷轧钢;两个(2)热浸镀锌钢面板;和十六(16)个电镀锌钢板。将所述面板浸入约 80 (28℃)的预处理浴液中两(2)分钟,并且适度搅拌。接着,将该面板用去离子水喷涂约 10-15 秒来冲洗,并且用温空气吹掉来干燥。

[0092] 在将第一组的 20 个面板穿过所述浴液加工后,使用上述方法测量每个预处理浴的锆水平、pH 和氟离子水平。

[0093] 基于这些测量,将 ZIRCOBOND R1 和实施例 1 的补充剂组合物加入到每个各自的浴液中,来将浴液的锆水平调整回到起始值。如果任何调整是必需的,则还进行了调整,来将 pH 调整到 4.4-4.8 和将游离氟离子水平调整到 40-70ppm。pH 是通过将 CHEMFIL BUFFER 加入到每个浴液中来调整的(如果需要)。游离氟离子是通过将 ZIRCOBOND 对照 #4 加入到每个浴液中来调整的(如果需要)。

[0094] 上述浴液贫化和补充方法在 20 个面板组中持续,直到总共 300 个面板已经在每个浴液中处理为止。记录了加入到每个浴液中的 ZIRCOBOND R1 和实施例 1 的补充剂组合物,CHEMFIL BUFFER 和 ZIRCOBOND 对照 #4 的量。还收集和测量了在浴液中形成的任何淤浆。结果显示在下表 2 中:

[0095] 表 2

[0096]

补充剂组合物	浴液化学用量(g)			所产生的淤浆(g)
	补充剂	Chemfil Buffer	Zircobond 对照#4	
ZIRCOBOND R1	54.3g	7.4g	8.7g	1.6g
实施例 1	48.9g	3.4g	3.1g	0.9g

[0097] 实施例 2

[0098] 补充剂组合物是如下来制备的。实施例 1 的补充剂组合物中所存在的每个成分的量反映在下表 1 中。每个百分比是用重量表达的。所存在的甲烷磺酸的量足以产生与通过碱式碳酸锆所提供的锆 4 :1 的化学计量比。

[0099] 表 3

[0100]

六氟锆酸,45%（获自 Honeywell）	17.58%
碱式碳酸锆（获自 Blue Line Corporation）	5.86%
甲烷磺酸（获自 Sigma-Aldrich Company）	7.42%
硝酸铜溶液,18%铜（获自 Shepherd Chemical）	7.6%
去离子水	余量

[0101] 除了实施例 1 所用的上述材料之外,使用了下面的材料 :

[0102] ZIRCOBOND ZRF,一种锆预处理整理产品,市售自 PPG Industries, Inc.

[0103] CHEMKLEEN 2010LP,碱性清洁产品,市售自 PPG Industries, Inc.

[0104] CHEMKLEEN 181ALP,碱性清洁产品,市售自 PPG Industries, Inc.

[0105] 一种新的锆预处理浴是使用在去离子水中 10.04g/L 的 ZIRCOBOND ZRF 来制备的。将该浴液的 pH 用 CHEMFIL BUFFER 调整到约 4.5。

[0106] 该预处理浴的四升等分部分是如下来测试的 :将面板在预处理浴中预处理来贫化它,如实施例 1 那样,然后将该浴液使用表 2 所述补充剂来调整。

[0107] 浴液中的锆和游离氟离子的初始水平是如实施例 1 所述来测量的。锆的水平是在 186ppm 测量的（作为元素金属来测量）。初始游离氟离子是在 128ppm 测量的。

[0108] 以与实施例 1 类似的方式如下来制备面板,用于穿过所述浴液来加工。通过在 CHEMKLEEN2010LP 的 1.25% v/v 溶液中用所加入的 0.125%的 CHEMKLEEN181ALP 喷涂来将所述面板清洁二 (2) 分钟。将该面板浸入去离子水中约十 (10) 秒,随后用去离子水喷涂约十 (10) 秒来冲洗。

[0109] 然后穿过所述浴液加工一组面板。该组由下面的组成 :八个 4”x12”热浸镀锌板 ;两个 4”x6”热浸镀锌板 ;一个 4”x6”铝板 (6111T43) ;和一个 4”x6”冷轧钢板。这个组的

表面积的量等于实施例 1 的面板组；锌涂覆的（镀锌的）与冷轧钢与铝的比率也相同，除了在这个实施例中，镀锌金属完全由热浸镀锌板组成。在约 73 (23℃）将所述面板浸入预处理浴中两 (2) 分钟，并且适度搅拌。接着，将该面板用去离子水喷涂约 10-15 秒来冲洗，并且用温空气吹掉来干燥。

[0110] 在将第一组的 20 个面板穿过所述浴液加工后，使用上述方法测量每个预处理浴的锆水平、pH 和氟离子水平。

[0111] 基于这些测量，将实施例 2 补充剂组合物加入到浴液中，来将浴液的锆水平调整回到起始值。如果任何调整是必需的，则还进行了调整，来将 pH 调整到 4.5-4.8 和将游离氟离子水平调整到 100-160ppm。pH 是通过将 CHEMFIL BUFFER 加入到浴液中来调整的（如果需要）。游离氟离子是通过将 ZIRCOBOND 对照 #4 加入到浴液中来调整的（如果需要）。

[0112] 在所述面板组中继续上述浴液贫化和补充方法，直到等价于 320 个 4”x6”面板或者 160 个 4”x12”面板（即，16 组面板）的表面积已经在浴液中处理为止。记录了加入到浴液中的实施例 2 的补充剂组合物，CHEMFIL BUFFER 和 ZIRCOBOND 对照 #4 的量。结果显示在下表 4 中：

[0113] 表 4

[0114]

补充剂组合物	浴液化学用量 (g)		
	补充剂	Chemfil Buffer	Zircobond 对照 #4
实施例 2	17.92g	2.2g	4.81g

[0115] 除去过量的游离氟离子和将游离氟离子保持在起始所必需的化学品的量因此明显小于实施例 1 所述的 ZIRCOBOND R1，即使所处理的金属的量稍高也是如此。

[0116] 虽然上面出于说明的目的而描述了本发明具体的实施方案，但是对本领域技术人员来说很显然可以对本发明的细节进行诸多的变化，而不脱离附加的权利要求所定义的本发明。