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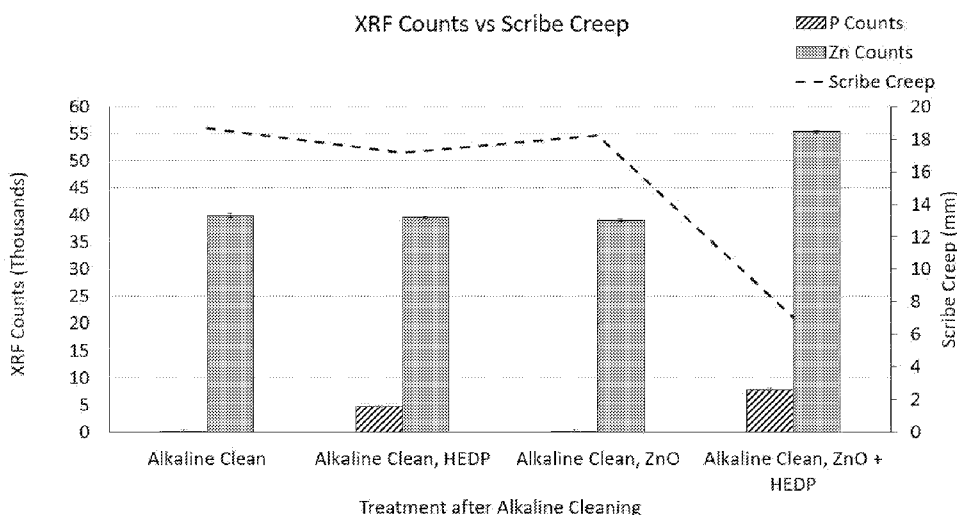
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(54) Title: SYSTEMS AND METHODS FOR TREATING A SUBSTRATE

FIG. 4



(57) Abstract: Disclosed herein are pretreatment compositions comprising at least 25 ppm of a phosphonate based on total weight of the pretreatment composition; at least 6 ppm of zinc based on total weight of the pretreatment composition; and a pH of 6.0 or less. Also disclosed herein are systems and methods for treating a substrate with one of the pretreatment compositions disclosed herein. Also disclosed are substrates that have been treated with one of the pretreatment compositions disclosed herein.



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## SYSTEMS AND METHODS FOR TREATING A SUBSTRATE

### GOVERNMENT CONTRACT

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### FIELD

**[0002]** The present disclosure relates to compositions, systems, and methods for treating a substrate.

### BACKGROUND

**[0003]** The use of protective coatings on metal substrates for improved corrosion resistance and paint adhesion is common. Conventional techniques for coating such substrates include techniques that involve pretreating the metal substrate with chromium-containing compositions. The use of such chromate-containing compositions, however, imparts environmental and health concerns.

### SUMMARY

**[0004]** Disclosed herein is a pretreatment composition comprising at least 25 ppm of a phosphonate based on total weight of the pretreatment composition; at least 6 ppm of zinc based on total weight of the pretreatment composition; and a pH of 6.0 or less.

**[0005]** Further disclosed herein is a system for treating a substrate comprising a cleaning composition; and one of the pretreatment compositions disclosed herein.

**[0006]** Further disclosed herein is a method of treating a substrate comprising contacting at least a portion of a substrate surface with one of the pretreatment compositions disclosed herein.

**[0007]** Further disclosed herein is a substrate treated with one of the pretreatment compositions disclosed herein.

**[0008]** Further disclosed herein is a substrate treated with the system and/or methods described herein.

### BRIEF DESCRIPTION OF THE FIGURES

**[0009]** FIG. 1 shows FIB-EDS-TEM of an Eform Plus magnesium substrate treated with Pretreatment 1 (PT 1) followed by an alkaline cleaner according to Example 2. FIG. 1A shows a high-angle annular diffraction TEM micrograph. FIGS. 1B – 1E are TEM micrographs overlaid with elemental maps (1B, magnesium; 1C, oxygen, 1D, phosphorous; 1E, zinc) as determined by EDS.

**[0010]** FIG. 2 shows FIB-EDS-TEM of an Eform Plus magnesium substrate treated with an alkaline cleaner and no pretreatment according to Example 2. FIGS. 2B – 2E show TEM micrographs overlaid with elemental maps (2B, magnesium; 2C, oxygen; 2D, phosphorous, 2E, zinc) as determined by EDS.

**[0011]** FIG. 3 shows an XPS depth profile of Eform Plus magnesium substrates treated with (3A) alkaline cleaner and no pretreatment, (3B) alkaline cleaner and PT 1 (ZnO + HEDP), (3C) alkaline cleaner and PT 7 (ZnO), and (3D) alkaline cleaner and PT 2 (HEDP) as a function of atomic percent.

**[0012]** FIG. 4 shows a bar graph showing the deposition of phosphorous and zinc (counts) measured using X-ray fluorescence (XRF) on Eform Plus magnesium panels treated with alkaline cleaner alone, alkaline cleaner and PT 2 (HEDP), alkaline cleaner and PT 7 (ZnO), and alkaline cleaner and PT 1 (ZnO + HEDP).

### DETAILED DESCRIPTION

**[0013]** For purposes of the following detailed description, it is to be understood that the disclosure may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers such as those expressing values, amounts, percentages, ranges, subranges, and fractions may be prefaced by the word “about,” even if the term does not expressly appear. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present disclosure. 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. When a closed or open-ended numerical range is described herein, all numbers, values, amounts, percentages, subranges, and fractions within or

encompassed by the numerical range are to be considered as being specifically included in and belonging to the original disclosure of this application as if these numbers, values, amounts, percentages, subranges, and fractions had been explicitly written out in their entirety.

**[0014]** Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the disclosure 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.

**[0015]** As used herein, unless indicated otherwise, a plural term can encompass its singular counterpart and vice versa, unless indicated otherwise. For example, although reference is made herein to “a” phosphonate or “an” organophosphonic acid, a combination (i.e., a plurality) of these compounds can be used.

**[0016]** 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.

**[0017]** As used herein, “including,” “containing,” and like terms are understood in the context of this application to be synonymous with “comprising” and are therefore open-ended and do not exclude the presence of additional undescribed or unrecited elements, materials, ingredients, or method steps. As used herein, “consisting of” is understood in the context of this application to exclude the presence of an unspecified element, ingredient, or method step. As used herein, “consisting essentially of” is understood in the context of this application to include the specified elements, materials, ingredients or method steps “and those that do not materially affect the basic and novel characteristic(s)” of what is being described.

**[0018]** As used herein, the terms “on,” “onto,” “applied on,” “applied onto,” “formed on,” “deposited on,” “deposited onto,” mean formed, overlaid, deposited, or provided on but not necessarily in contact with the surface. For example, a coating composition “applied onto” a substrate does not preclude the presence of one or more other intervening coating layers of the same or different composition located between the coating composition and the substrate.

**[0019]** As used herein, a “system” refers to a plurality of treatment compositions (including cleaners and rinses) used to treat a substrate and to produce a treated substrate. The system may be part of a production line (such as a factory production line) that produces a finished substrate or a treated substrate that is suitable for use in other production lines.

**[0020]** As used herein, a “salt” refers to an ionic compound made of metal cations and non-metal anions and having an overall electrical charge of zero. Salts may be hydrated or anhydrous.

**[0021]** As used herein, “composition” refers to a solution or dispersion and “aqueous composition” refers to a composition in a medium that comprises predominately water. For example, the aqueous medium may comprise water in an amount of more than 50 wt.%, or more than 70 wt.%, or more than 80 wt.%, or more than 90 wt.%, or more than 95 wt.% based on the total weight of the medium. That is, the aqueous medium may, for example, consist substantially of water.

**[0022]** As used herein, the term “dispersion” refers to a two-phase transparent, translucent, or opaque system in which a discontinuous phase, e.g., metal particles, are dispersed in a continuous phase such as an aqueous medium, which includes water.

**[0023]** As used herein, the term “derivative” refers to a compound that may arise from another compound if one atom or group of atoms is replaced with another atom or group of atoms. For example, a derivative of etidronic acid may arise from replacing a hydroxide group with an alkoxide group.

**[0024]** As used herein, “pretreatment composition” refers to a composition that is capable of reacting with and chemically altering the substrate surface and binding to it to form a film that affords corrosion protection.

**[0025]** As used herein, “pretreatment bath” refers to an aqueous bath containing the pretreatment composition and that may contain components that are byproducts of the process.

**[0026]** As used herein, a “coating composition” refers to a composition, e.g., a solution, a mixture, or a dispersion, that, in an at least partially dried or cured state, is capable of producing a film, layer, or the like on at least a portion of a substrate surface.

**[0027]** As further defined herein, ambient conditions generally refer to room temperature and humidity conditions or temperature and humidity conditions that are typically found in the area in which a composition is being applied to a substrate, e.g., at 10°C to 32°C and 5% to 80% relative humidity, while slightly thermal conditions are temperatures that are slightly above ambient temperature (e.g., greater than 32°C to 40°C).

**[0028]** As used herein, unless indicated otherwise, the term “substantially free” means that a particular material is not purposefully added to a mixture or composition, respectively, and

is only present as an impurity in a trace amount of 5 ppm or less based on a total weight of the mixture or composition, respectively. As used herein, unless indicated otherwise, the term “essentially free” means that a particular material is only present in an amount of 1 ppm or less based on a total weight of the mixture or composition, respectively. As used herein, unless indicated otherwise, the term “completely free” means that a mixture or composition, respectively, does not comprise a particular material, i.e., the mixture or composition comprises 1 ppb or less of such material based on a total weight of the mixture or composition, or that such material is below the detection limit of common analytical techniques.

**[0029]** Unless otherwise disclosed herein, as used herein, the terms “total composition weight,” “total weight of a composition,” or similar terms refer to the total weight of all ingredients being present in the respective composition including any solvents.

**[0030]** As used herein, “phosphonates” are compounds comprising C-PO(OR)<sub>2</sub> groups, wherein R may independently be an alkyl group, an aryl group, or an H.

**[0031]** As used herein, “phosphonic acids” are compounds comprising C-PO(OH)<sub>2</sub> or C-PO(OR)<sub>2</sub> groups, wherein R may be an H, an alkyl group, or an aryl group, wherein at least one R comprises an H.

**[0032]** As used herein, “monophosphonic acid” means a compound that has one phosphonic acid moiety.

**[0033]** As used herein, “diphosphonic acid” means a compound that has two phosphonic acid moieties.

**[0034]** As used herein, “polyphosphonic acid” means a compound having more than two phosphonic acid moieties.

**[0035]** As used herein, “organic compounds” means compounds that comprise at least one covalent bond between a carbon and another element, such as another carbon, hydrogen, oxygen, and/or nitrogen.

**[0036]** As used herein, “organic compounds other than phosphonates or phosphonic acids” means an organic compound that is not a phosphonate or a phosphonic acid. compound comprising C-PO(OR)<sub>2</sub> groups, wherein R may be an alkyl group, an aryl group, or an H and/or phosphonic acids comprising C-PO(OH)<sub>2</sub> or C-PO(OR)<sub>2</sub> groups, wherein R may be an H, an alkyl group, or an aryl group, wherein at least one R comprises an H.

**[0037]** As used herein, “alkaline” means a composition comprising a pH greater than 7.0.

**[0038]** As mentioned above, the present disclosure is directed to a pretreatment composition, the pretreatment composition comprising, consisting essentially of, or consisting of at least 25 ppm of a phosphonate based on total weight of the pretreatment composition; 6 ppm of zinc based on total weight of the pretreatment composition; and a pH of 6.0 or less.

**[0039]** As stated above, the pretreatment composition may comprise a phosphonate. The molecular weight (Mw) of the phosphonate may be at least 100 g/mol, such as at least 200 g/mol, such as at least 1,000 g/mol, such as at least 1,500 g/mol, such as at least 10,000 g/mol, such as at least 15,000 g/mol. The Mw of the phosphonate may be no more than 50,000 g/mol, such as no more than 40,000 g/mol, such as no more than 30,000 g/mol, such as no more than 1,000 g/mol, such as no more than 600 g/mol. The Mw of the phosphonate may be 100 g/mol to 50,000 g/mol, such as 100 g/mol to 1,000 g/mol, such as 100 g/mol to 600 g/mol, such as 200 g/mol to 1,000 g/mol, such as 200 g/mol to 600 g/mol, such as 1,000 g/mol to 40,000 g/mol, such as 1,500 g/mol to 50,000 g/mol, such as 1,500 g/mol to 30,000 g/mol, such as 10,000 g/mol to 50,000 g/mol, such as 15,000 g/mol to 40,000 g/mol. As used herein, "Mw" refers to the weight average molecular weight as determined by Gel Permeation Chromatography using Waters 2695 separation module with a Waters 410 differential refractometer (RI detector), using polystyrene standards, tetrahydrofuran (THF) as the eluent at a flow rate of 1 ml min<sup>-1</sup>, and two PL Gel Mixed C columns for separation.

**[0040]** The phosphonate may comprise at least 1 carbon atom, such as at least 5 carbon atoms, such as at least 25 carbon atoms, such as at least 150 carbon atoms, such as at least 200 carbon atoms. The phosphonate may comprise no more than 1,000 carbon atoms, such as no more than 750 carbon atoms, such as no more than 50 carbon atoms, such as no more than 15 carbon atoms. The phosphonate may comprise 1 to 1,000 carbon atoms, such as 1 to 15 carbon atoms, such as 5 to 50 carbon atoms, such as 25 to 1,000 carbon atoms, such as 150 to 1,000 carbon atoms, such as 200 to 750 carbon atoms.

**[0041]** The phosphonate may comprise a phosphonic acid. The phosphonic acid may comprise a monophosphonic acid, a diphosphonic acid, a polyphosphonic acid, or combinations thereof. In examples, the diphosphonic acid may comprise etidronic acid or derivatives thereof. Other suitable phosphonic acids may comprise ethylenediamine tetra(methylenephosphonic) acid (EDTMP), diethylenetriaminepenta(methylene-phosphonic acid) (DTPMPA), iminodi(methylphosphonic acid), N-(phosphonomethyl)iminodiacetic acid hydrate,



(aminomethyl)phosphonic acid, glyphosate, methylenediphosphonic acid, N,N-bis(phosphonomethyl)glycine, glyphosine, 2-phosphono 1,2,4-butane tricarboxylic acid (PBTC), aminotris(methylenephosphonic acid) (ATMP aminotris), polyvinylphosphonic acid (PVPA), or combinations thereof.

**[0042]** The pretreatment composition may comprise the phosphonate in an amount of at least 25 ppm based on total weight of the pretreatment composition, such as at least 30 ppm, such as at least 40 ppm, such as at least 500 ppm, such as at least 2,000 ppm, such as at least 4,000 ppm. The pretreatment composition may comprise the phosphonate in an amount of no more than 60,000 ppm based on total weight of the pretreatment composition, such as no more than 55,000 ppm, such as no more than 50,000 ppm. The pretreatment composition may comprise the phosphonate in an amount of 25 ppm to 60,000 ppm based on total weight of the pretreatment composition, such as 30 ppm to 55,000 ppm, such as 40 ppm to 50,000 ppm, such as 500 ppm to 55,000 ppm, such as 2,000 ppm to 55,000 ppm, such as 4,000 ppm to 55,000 ppm, such as 500 ppm to 50,000 ppm, such as 2,000 ppm to 50,000 ppm, such as 4,000 ppm to 50,000 ppm.

**[0043]** As stated above, the pretreatment composition may comprise zinc. The zinc may be provided in the form of a compound comprising zinc or a salt comprising zinc, or a combination thereof. Suitable compounds of zinc include, but are not limited to, zinc oxide, zinc hydroxide, zinc nitrate, zinc sulfate, zinc chloride, zinc chlorate, or combinations thereof.

**[0044]** The pretreatment composition may comprise zinc in an amount of at least 6 ppm based on total weight of the pretreatment composition, such as at least 100 ppm, such as at least 500 ppm, such as at least 1,000 ppm, such as at least 1,500 ppm. The pretreatment composition may comprise zinc in an amount of no more than 15,000 ppm based on total weight of the pretreatment composition, such as no more than 12,000 ppm, such as no more than 10,000 ppm, such as no more than 7,500 ppm. The pretreatment composition may comprise zinc in an amount of 6 ppm to 15,000 ppm based on total weight of the pretreatment composition, such as 100 ppm to 15,000 ppm, such as 100 ppm to 12,000 ppm, such as 100 ppm to 10,000 ppm, such as 100 ppm to 7,500 ppm, such as 500 ppm to 12,000 ppm, such as 500 ppm to 10,000 ppm, such as 750 ppm to 7,500 ppm, such as 1,000 ppm to 10,000 ppm, such as 1,500 ppm to 7,500 ppm.

**[0045]** As stated above, the pretreatment composition may comprise free fluoride. As used herein, “free fluoride” refers to fluoride present in the pretreatment composition that is not

bound to metal ions or hydrogen ions, as measured in parts per million of fluoride. Free fluoride may be measured using, for example, an Orion Dual Star Dual Channel Benchtop Meter equipped with a fluoride ion selective electrode (“ISE”) available from Thermoscientific, the symphony® Fluoride Ion Selective Combination Electrode supplied by VWR International, or similar electrodes. See, e.g., Light and Cappuccino, *Determination of fluoride in toothpaste using an ion-selective electrode*, J. Chem. Educ., 52:4, 247-50, April 1975. The fluoride ISE may be standardized by immersing the electrode into solutions of known fluoride concentration and recording the reading in millivolts, and then plotting these millivolt readings in a logarithmic graph. The millivolt reading of an unknown sample can then be compared to this calibration graph and the concentration of fluoride determined. Alternatively, the fluoride ISE can be used with a meter that will perform the calibration calculations internally and thus, after calibration, the concentration of the unknown sample may be read directly. Examples of compounds to be added to adjust the fluoride level include, but are not limited to, ammonium bifluoride, potassium hydrogen fluoride, and yttrium nitrate.

**[0046]** The pretreatment composition may comprise free fluoride in an amount of at least 15 ppm based on a total weight of the pretreatment composition, such as at least 50 ppm, such as at least 100 ppm, such as at least 150 ppm, such as at least 200 ppm. The pretreatment composition may comprise free fluoride in an amount of no more than 750 ppm based on a total weight of the pretreatment composition, such as no more than 700 ppm, such as no more than 650 ppm, such as no more than 600 ppm, such as no more than 550 ppm. The pretreatment composition may comprise free fluoride in an amount of 15 ppm to 750 ppm free fluoride based on a total weight of the pretreatment composition, such as 50 ppm to 700 ppm, such as 100 ppm to 650 ppm, such as 150 ppm to 600 ppm, such as 200 ppm to 550 ppm.

**[0047]** In examples, pretreatment composition may comprise a pH of 6.0 or less, such as 5.0 or less, such as 4.0 or less. The pretreatment composition may comprise a pH of at least 0.3, such as at least 0.5, such as at least 0.8, such as at least 0.9, such as at least 1.0, such as at least 1.5, such as at least 2.0. The pretreatment composition may comprise a pH of 0.3 to 6.0, such as 0.3 to 5.0, such as 0.3 to 4.0, such as 0.5 to 6.0, such as 0.5 to 5.0, such as 0.5 to 4.0, such as 0.8 to 6.0, such as 0.8 to 5.0, such as 0.8 to 4.0, such as 1.0 to 6.0, such as 1.0 to 5.0, such as 1.0 to 4.0, such as 1.5 to 4.0, such as 2.0 to 4.0. The pH may be adjusted using, for example, any acid/base as is necessary. The pH of the pretreatment composition may be maintained through

the inclusion of an acidic material, including water soluble and/or water dispersible acids, such as nitric acid, sulfuric acid, and/or phosphoric acid. The pH of the composition may be 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 diisopropanolamine, triethylamine, dimethylethanolamine, 2-amino-2methylpropanol, methylethyl amine, or combinations thereof. The base can partially or completely neutralize the phosphonate compounds to enhance the solubility of the phosphonate compounds.

**[0048]** The pretreatment composition may exclude chromium or chromium-containing compounds. That is, the pretreatment composition and/or coatings or layers deposited from the pretreatment composition may be substantially free, may be essentially free, and/or may be completely free of such chromium or chromium-containing compounds. As used herein, the term “chromium-containing compounds” refers to materials that include trivalent and/or hexavalent chromium. 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, strontium dichromate, chromium (III) sulfate, chromium (III) chloride, and chromium (III) nitrate. When a pretreatment composition or a material deposited onto a substrate surface by deposition of the pretreatment composition is substantially free, essentially free, or completely free of chromium, this includes chromium in any form, such as, but not limited to, the trivalent and hexavalent chromium-containing compounds listed above.

**[0049]** Thus, optionally, the pretreatment compositions and/or material deposited on a substrate surface from the pretreatment composition may be substantially free, may be essentially free, and/or may be completely free of one or more of any of the elements or compounds in the preceding paragraph. Accordingly, material formed on a substrate surface from the pretreatment composition may be substantially free of chromium or derivatives thereof meaning that chromium or derivatives thereof are not intentionally added, but may be present in trace amounts, such as because of impurities or unavoidable contamination from the environment. In other words, the amount of material is so small that it does not affect the properties of the pretreatment composition or deposited material; in the case of chromium, this may further include that the element or compounds thereof are not present in the pretreatment

compositions and/or deposited material in such a level that it causes a burden on the environment. The term “substantially free,” when used with respect to chromium, means that the pretreatment composition and/or deposited material contains less than 10 ppm of any or all of the elements or compounds listed in the preceding paragraph based on total weight of the composition or the layer, respectively, if any at all. The term “essentially free,” when used with respect to chromium, means that the pretreatment compositions and/or deposited material contains less than 1 ppm of any or all of the elements or compounds listed in the preceding paragraph, if any at all. The term “completely free,” when used with respect to chromium, means that the pretreatment composition comprises 0 ppm of such material or that such material is below the detection limit of common analytical techniques.

**[0050]** The pretreatment composition may be substantially free, essentially free, or completely free of organic compounds other than phosphonates or phosphonic acids.

**[0051]** The pretreatment composition may comprise a carrier, often an aqueous medium, so that the pretreatment composition is in the form of a solution or dispersion. For example, the pretreatment composition may be an aqueous composition.

**[0052]** The pretreatment composition may optionally contain other materials in addition to those described above, such as surfactants and other auxiliaries conventionally used in the art of pretreatment. In an aqueous medium, water-soluble organic solvents, for example, alcohols with up to above 8 carbon atoms, such as methanol, isopropanol, 1-methoxy-2-propanol, and the like, may be present; or glycol ethers such as the monoalkyl ethers of ethylene glycol, diethylene glycol, or propylene glycol, and the like; dimethylformamide; xylene; and combinations thereof. When present, water dispersible organic solvents are typically used in amounts up to about ten percent by volume, based on the total volume of the pretreatment, as the case may be. Other optional materials include surfactants that function as defoamers or substrate wetting agents. Anionic, cationic, amphoteric and/or nonionic surfactants may be used.

**[0053]** The pretreatment composition optionally may comprise 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, chlorate ions, and chlorite ions, as well as ascorbic acid, citric acid, tartaric acid, malonic acid, succinic acid and salts thereof.

**[0054]** The pretreatment composition also may comprise a resinous binder. Suitable resins include reaction products of one or more alkanolamines and an epoxy-functional material containing at least two epoxy groups, such as those disclosed in United States Patent No. 5,653,823, incorporated herein by reference. In some cases, such resins contain beta hydroxy ester, imide, or sulfide functionality, incorporated by using dimethylolpropionic acid, phthalimide, or mercaptoglycerine as an additional reactant in the preparation of the resin. Alternatively, the reaction product is that of the diglycidyl ether of Bisphenol A (commercially available from Shell Chemical Company as EPON 880), dimethylol propionic acid, and diethanolamine in a 0.6 to 5.0:0.05 to 5.5:1 mole ratio. Other suitable resinous binders include water soluble and water dispersible polyacrylic acids as disclosed in United States Patent Nos. 3,912,548 and 5,328,525, disclosed herein by reference; phenol formaldehyde resins as described in United States Patent No. 5,662,746, disclosed herein by reference; water soluble polyamides such as those disclosed in WO 95/33869, disclosed herein by reference; copolymers of maleic or acrylic acid with allyl ether as described in Canadian patent application 2,087,352, disclosed herein by reference; and water soluble and dispersible resins including epoxy resins, aminoplasts, phenol-formaldehyde resins, tannins, and polyvinyl phenols as discussed in United States Patent No. 5,449,415, disclosed herein by reference.

**[0055]** If used, the pretreatment composition may comprise the resinous binder in an amount of 0.005 percent to 30 percent by weight, such as 0.5 to 3 percent by weight, based on the total weight of the pretreatment composition.

**[0056]** Alternatively, the pretreatment composition may be substantially free or, in some cases, completely free of any resinous binder. As used herein, the term “substantially free,” when used in reference to the absence of resinous binder in the pretreatment composition, means that any resinous binder is present in the pretreatment composition in a trace amount of less than 0.005 percent by weight. As used herein, the term “completely free” means that there is no resinous binder in the pretreatment composition at all.

#### System

**[0057]** The present disclosure also is directed to a system for treating a substrate. The system may comprise, or may consist essentially of, or may consist of, a cleaning composition and a pretreatment composition disclosed herein. The pretreatment composition can be any pretreatment composition as described herein. For example, the system may comprise, or may

consist essentially of, or may consist of a cleaning composition; and a pretreatment composition comprising, or consisting essentially of, or consisting of, at least 25 ppm of a phosphonate based on total weight of the pretreatment composition, at least 6 ppm of zinc based on total weight of the pretreatment composition, and a pH of 6.0 or less.

**[0058]** The cleaning composition may be an alkaline cleaning composition. Examples of suitable alkaline cleaners include Chemkleen™ 166HP, 166M/C, 177, 181ALP, 490MX, 2010LP, and Surface Prep 1 (SP1), Ultrax 32, Ultrax 97, Ultrax 29, and Ultrax92D, each of which are commercially available from PPG Industries, Inc. (Cleveland, OH), and any of the DFM Series, RECC 1001, and 88X1002 cleaners (commercially available from PRC-DeSoto International, Sylmar, CA), and Turco 4215-NCLT and Ridolene (commercially available from Henkel Technologies, Madison Heights, MI).

**[0059]** The cleaning composition may comprise a pH of at least 10.0, such as at least 10.5.

**[0060]** The system of the present disclosure may further comprise, or may consist essentially of, or may consist of, a film-forming composition. The film-forming composition may comprise, or may consist essentially of, or may consist of, a coating composition. The coating composition may comprise, or consist essentially of, or consist of, a film-forming resin. Any suitable technique may be used to deposit such a coating composition onto the substrate including, for example, brushing, dipping, flow coating, spraying and the like. Optionally, however, as described in more detail below, such depositing of a coating composition may comprise an electrocoating step wherein an electrodepositable coating composition is deposited onto a metal substrate by electrodeposition. In certain other instances, as described in more detail below, such depositing of a coating composition comprises a powder coating step. In still other instances, the coating composition may be a liquid coating composition.

**[0061]** The coating composition may comprise a thermosetting film-forming resin or a thermoplastic film-forming resin. As used herein, the term “film-forming resin” refers to resins that can form a self-supporting continuous film on at least a horizontal surface of a substrate upon removal of any diluents or carriers present in the composition and/or upon curing at ambient or elevated temperature. Conventional film-forming resins that may be used include, without limitation, those typically used in automotive OEM coating compositions, automotive refinish coating compositions, industrial coating compositions, architectural coating

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

**[0062]** As previously indicated, the coating composition may be an electrodepositable coating composition comprising a water-dispersible, ionic salt group-containing film-forming resin that may be deposited onto the substrate by an electrocoating step wherein the electrodepositable coating composition is deposited onto the metal substrate under the influence of an applied electrical potential, i.e., by electrodeposition. The ionic salt group-containing film-forming polymer may comprise a cationic salt group containing film-forming polymer for use in a cationic electrodepositable coating composition. As used herein, the term “cationic salt group-containing film-forming polymer” refers to polymers that include at least partially neutralized cationic groups, such as sulfonium groups and ammonium groups, that impart a positive charge. The cationic salt group-containing film-forming polymer may comprise active hydrogen functional groups, including, for example, hydroxyl groups, primary or secondary amino groups, and thiol groups. Cationic salt group-containing film-forming polymers that comprise active hydrogen functional groups may be referred to as active hydrogen-containing, cationic salt group-containing film-forming polymers. Examples of polymers that are suitable for use as the cationic salt group-containing film-forming polymer include, but are not limited to, alkyd polymers, acrylics, polyepoxides, polyamides, polyurethanes, polyureas, polyethers, and polyesters, among others. The cationic salt group-containing film-forming polymer may be present in the cationic electrodepositable coating composition in an amount of 40% to 90% by weight, such as 50% to 80% by weight, such as 60% to 75% by weight based on the total weight of the resin solids of the electrodepositable coating composition. As used herein, the “resin solids” include the ionic salt group-containing film-forming polymer, curing agent (as discussed

below), and any additional water-dispersible non-pigmented component(s) present in the electrodepositable coating composition.

**[0063]** Alternatively, the ionic salt group containing film-forming polymer may comprise an anionic salt group containing film-forming polymer for use in an anionic electrodepositable coating composition. As used herein, the term “anionic salt group containing film-forming polymer” refers to an anionic polymer comprising at least partially neutralized anionic functional groups, such as carboxylic acid and phosphoric acid groups that impart a negative charge. The anionic salt group-containing film-forming polymer may comprise active hydrogen functional groups. Anionic salt group-containing film-forming polymers that comprise active hydrogen functional groups may be referred to as active hydrogen-containing, anionic salt group-containing film-forming polymers. The anionic salt group-containing film-forming polymer may comprise base-solubilized, carboxylic acid group-containing film-forming polymers such as the reaction product or adduct of a drying oil or semi-drying fatty acid ester with a dicarboxylic acid or anhydride; and the reaction product of a fatty acid ester, unsaturated acid or anhydride and any additional unsaturated modifying materials which are further reacted with polyol. Also suitable are the at least partially neutralized interpolymers of hydroxy-alkyl esters of unsaturated carboxylic acids, unsaturated carboxylic acid and at least one other ethylenically unsaturated monomer. Still another suitable anionic electrodepositable resin comprises an alkyd-aminoplast vehicle, i.e., a vehicle containing an alkyd resin and an amine-aldehyde resin. Another suitable anionic electrodepositable resin composition comprises mixed esters of a resinous polyol. Other acid functional polymers may also be used such as phosphatized polyepoxide or phosphatized acrylic polymers. Exemplary phosphatized polyepoxides are disclosed in United States Patent Application Publication No. 2009/0045071 at [0004]-[0015] and United States Patent Application Serial No. 13/232,093 at [0014]-[0040], the cited portions of which being incorporated herein by reference. The anionic salt group-containing film-forming polymer may be present in the anionic electrodepositable coating composition in an amount of 50% to 90%, such as 55% to 80%, such as 60% to 75% based on the total weight of the resin solids of the electrodepositable coating composition.

**[0064]** The electrodepositable coating composition may further comprise a curing agent. The curing agent may comprise functional groups that are reactive with the functional groups, such as active hydrogen groups, of the ionic salt group-containing film-forming polymer to



effectuate cure of the coating composition to form a coating. Non-limiting examples of suitable curing agents are at least partially blocked polyisocyanates, aminoplast resins and phenoplast resins, such as phenolformaldehyde condensates including allyl ether derivatives thereof. The curing agent may be present in the cationic electrodepositable coating composition in an amount of 10% to 60% by weight, such as 20% to 50% by weight, such as 25% to 40% by weight based on the total weight of the resin solids of the electrodepositable coating composition.

Alternatively, the curing agent may be present in the anionic electrodepositable coating composition in an amount of 10% to 50% by weight, such as 20% to 45% by weight, such as 25% to 40% by weight based on the total weight of the resin solids of the electrodepositable coating composition.

**[0065]** The electrodepositable coating composition may further comprise other optional ingredients, such as a pigment composition and, if desired, various additives such as fillers, plasticizers, antioxidants, biocides, UV light absorbers and stabilizers, hindered amine light stabilizers, defoamers, fungicides, dispersing aids, flow control agents, surfactants, wetting agents, or combinations thereof.

**[0066]** The electrodepositable coating composition may comprise water and/or one or more organic solvent(s). Water can for example be present in amounts of 40% to 90% by weight, such as 50% to 75% by weight based on total weight of the electrodepositable coating composition. If used, the organic solvents may typically be present in an amount of less than 10% by weight, such as less than 5% by weight based on total weight of the electrodepositable coating composition. The electrodepositable coating composition may in particular be provided in the form of an aqueous dispersion. The total solids content of the electrodepositable coating composition may be from 1% to 50% by weight, such as 5% to 40% by weight, such as 5% to 20% by weight based on the total weight of the electrodepositable coating composition. As used herein, "total solids" refers to the non-volatile content of the electrodepositable coating composition, i.e., materials which will not volatilize when heated to 110°C for 15 minutes.

**[0067]** The cationic electrodepositable coating composition may be deposited upon an electrically conductive substrate by placing the composition in contact with an electrically conductive cathode and an electrically conductive anode, with the surface to be coated being the cathode. Alternatively, the anionic electrodepositable coating composition may be deposited upon an electrically conductive substrate by placing the composition in contact with an

electrically conductive cathode and an electrically conductive anode, with the surface to be coated being the anode. An adherent film of the electrodeposable coating composition is deposited in a substantially continuous manner on the cathode or anode, respectively, when a sufficient voltage is impressed between the electrodes. The applied voltage may be varied and can be, for example, as low as one volt to as high as several thousand volts, such as between 50 and 500 volts. Current density is usually between 1.0 ampere and 15 amperes per square foot (10.8 to 161.5 amperes per square meter) and tends to decrease quickly during the electrodeposition process, indicating formation of a continuous self-insulating film.

**[0068]** Once the cationic or anionic electrodeposable coating composition is electrodeposited over at least a portion of the electroconductive substrate, the coated substrate may be heated to a temperature and for a time sufficient to cure the electrodeposited coating on the substrate. For cationic electrodeposition, the coated substrate may be heated to a temperature ranging from 230°F to 450°F (110°C to 232.2°C), such as from 275°F to 400°F (135°C to 204.4°C), such as from 300°F to 360°F (149°C to 180°C), such as 200°F to 210.2°F (93°C to 99°C). The curing time may be dependent upon the curing temperature as well as other variables, for example, the film thickness of the electrodeposited coating, level and type of catalyst present in the composition and the like. For example, the curing time can range from 10 minutes to 60 minutes, such as 20 minutes to 40 minutes. The thickness of the resultant cured electrodeposited coating may range from 10 to 50 microns.

**[0069]** Alternatively, as mentioned above, after the substrate has been contacted with the pretreatment compositions as described above, a powder coating composition may then be deposited onto at least a portion of the pretreated substrate surface. As used herein, “powder coating composition” refers to a coating composition in the form of a co-reactable solid in particulate form which is substantially or completely free of water and/or solvent. Accordingly, the powder coating composition disclosed herein is not synonymous to waterborne and/or solvent-borne coating compositions known in the art. The powder coating composition may comprise (a) a film forming polymer having a reactive functional group; and (b) a curing agent having a functional group that is reactive with the functional group of the film-forming polymer. Examples of powder coating compositions that may be used in the present disclosure include the polyester-based ENVIROCRON line of powder coating compositions (commercially available from PPG Industries, Inc.) or epoxy-polyester hybrid powder coating compositions. Alternative

examples of powder coating compositions that may be used include low temperature cure thermosetting powder coating compositions comprising (a) at least one tertiary aminourea compound, at least one tertiary aminourethane compound, or mixtures thereof, and (b) at least one film-forming epoxy-containing resin and/or at least one siloxane-containing resin (such as those described in United States Patent No. 7,470,752, assigned to PPG Industries, Inc. and incorporated herein by reference); and those comprising a solid particulate mixture of a reactive group-containing polymer having a  $T_g$  of at least 30°C (such as those described in United States Patent No. 6,797,387, assigned to PPG Industries, Inc. and incorporated herein by reference). The powder coating compositions are often applied by spraying, electrostatic spraying, or by the use of a fluidized bed. Other standard methods for coating application of the powder coating also can be employed such as brushing, dipping or flowing. After application of the powder coating composition, the coating is often heated to cure the deposited composition. The heating or curing operation is often carried out at a temperature in the range of from 130°C to 220°C, such as from 170°C to 190°C, for a period of time ranging from 10 minutes to 30 minutes, such as 15 minutes to 25 minutes. The thickness of the resultant film is typically from 50 microns to 125 microns.

**[0070]** As mentioned above, after the substrate has been contacted with the pretreatment compositions as described above, a liquid coating composition may then be applied or deposited onto at least a portion of the substrate surface. As used herein, “liquid coating composition” refers to a coating composition which contains a portion of water and/or solvent that may be substantially or completely removed from the composition upon drying and/or curing. Accordingly, the liquid coating composition disclosed herein is synonymous to waterborne and/or solvent-borne coating compositions known in the art.

**[0071]** The liquid coating composition may comprise, for example, (a) a film-forming polymer having a reactive functional group; and (b) a curing agent having a functional group that is reactive with the functional group or the film-forming polymer. In other examples, the liquid coating may contain a film forming polymer that may react with oxygen in the air or coalesce into a film with the evaporation of water and/or solvents. These film-forming mechanisms may require or be accelerated by the application of heat or some type of radiation such as Ultraviolet or Infrared. Examples of liquid coating compositions that may be used include the SPECTRACRON<sup>®</sup> line of solvent-based coating compositions, the AQUACRON<sup>®</sup> line of water-

based coating compositions, and the RAYCRON<sup>®</sup> line of UV cured coatings (all commercially available from PPG Industries, Inc.). Suitable film forming polymers that may be used in the liquid coating composition may comprise a (poly)ester, an alkyd, a (poly)urethane, an isocyanate, a (poly)urea, a (poly)epoxy, an anhydride, an acrylic, a (poly)ether, a (poly)sulfide, a (poly)amine, a (poly)amide, a (poly)vinyl chloride, a (poly)olefin, a (poly)vinylidene fluoride, a (poly)siloxane, or combinations thereof.

**[0072]** The film-forming resin may, in examples, be a primer composition and/or a topcoat composition. The primer and/or topcoat compositions may be, for example, chromate-based primers and/or advanced performance topcoats. The topcoats can be any of the described herein below. The primer coat can be a conventional chromate-based primer coat, such as those available from PPG Industries, Inc. (product code 44GN072), or a chrome-free primer such as those available from PPG (DESOPRIME CA7502, DESOPRIME CA7521, Deft 02Gn083, Deft 02GN084). Alternatively, the primer coat can be a chromate-free primer coat, such as the coating compositions described in United States Patent Application Serial No. 10/758,973, titled “CORROSION RESISTANT COATINGS CONTAINING CARBON”, and United States Patent Application Serial Nos. 10/758,972, and 10/346,374, both titled “CORROSION RESISTANT COATINGS”, all of which are incorporated herein by reference. Other chrome-free primers that are known in the art, and which can pass the military requirement of MIL-PRF-85582 Class N or MIL-PRF-23377 Class N, may also be used with the current disclosure.

#### Method

**[0073]** The present disclosure also is directed to a method for treating a substrate. The method may comprise, or may consist essentially of, or may consist of, contacting at least a portion of the substrate surface with a pretreatment composition disclosed herein.

**[0074]** In examples, the solution or dispersion of the pretreatment composition may be spontaneously applied or contacted to the substrate surface. For example, the solution or dispersion of the pretreatment composition may be brought into contact with the substrate by any of a variety of known techniques, such as dipping or immersion, spraying, intermittent spraying, dipping followed by spraying, spraying followed by dipping, brushing, or roll-coating. According to the disclosure, the solution or dispersion may be in contact with at least a portion of the substrate surface for at least 5 seconds, such as at least 45 seconds, such as at least 60 seconds, such as at least 120 seconds, such as at least 180 seconds, such as no more than 5

minutes. The contacting may be for 5 seconds to 5 minutes, such as 30 seconds to 5 minutes, such as 30 seconds to 4 minutes, such as 30 seconds to 3 minutes. The pretreatment composition may be maintained (during contacting) at ambient temperature or higher, such as at least 21°C (70°F), such as at least 24°C (75°F), such as at least 26°C (80°F), such as at least 32°C (90°F), such as at least 37°C (100°F), such as at least 43°C (110°F), such as at least 48°C (120°F), such as 21°C (70°F) to 48°C (120°F). As used herein, “spontaneous” or “spontaneously”, when used with respect to a pretreatment composition, refers to a pretreatment composition that is capable of reacting with and chemically altering the substrate surface and binding to it to form a protective layer in the absence of an externally applied voltage.

**[0075]** The method may further comprise contacting at least a portion of the substrate surface with a cleaning composition prior to contacting with the pretreatment composition disclosed herein. The cleaning composition can be any cleaning composition as discussed above in the context of the system disclosed herein.

**[0076]** The method may comprise, or may consist essentially of, or may consist of, contacting at least a portion of a surface of the substrate with a cleaning composition; and then contacting at least a portion of the surface with a pretreatment composition. The cleaning composition may comprise an alkaline pH. Optionally, the substrate surface may not be contacted with a surface treatment composition (excluding water rinses) prior to contacting the substrate surface with the pretreatment composition. As described more fully herein, in some instances, there may be rinse steps that intervene the contacting with the cleaning composition and the pretreatment composition. As used herein, “surface treatment” refers to treatment or contact of a substrate surface with a surface treatment composition or dispersion that comprises ingredients other than or in addition to water.

**[0077]** At least a portion of the substrate surface may be cleaned prior to contacting at least a portion of the substrate surface with one of the pretreatment compositions described above in order to remove grease, dirt, and/or other extraneous matter. At least a portion of the surface of the substrate may be cleaned by physical and/or chemical means, such as mechanically abrading the surface and/or cleaning/degreasing the surface with commercially available alkaline cleaning agents that are well known to those skilled in the art. Such cleaners are often preceded and/or followed by a water rinse, such as with tap water, distilled water, or combinations thereof.

**[0078]** Following the cleaning step(s), the substrate optionally may be rinsed with tap water, deionized water, and/or an aqueous solution of rinsing agents in order to remove any residue. The wet substrate surface may be treated with one of the pretreatment compositions described above or the substrate may be dried prior to treating the substrate surface, such as air dried, for example, by using an air knife, by flashing off the water by brief exposure of the substrate to a high temperature, such as 15°C to 100°C, such as 20°C to 90°C, or in a heater assembly using, for example, infrared heat, such as for 10 minutes at 70°C, or by passing the substrate between squeegee rolls.

**[0079]** The method may further comprise, or may consist essentially of, or may consist of contacting at least a portion of the surface of the substrate with a coating composition following the contacting with the pretreatment composition. The coating composition can be any coating composition as discussed above in the context of the system disclosed herein. The coating composition may comprise, or may consist essentially of, or may consist of a film-forming resin. The coating composition may, for example, be applied by electrodeposition, as detailed above.

#### Substrate

**[0080]** The present disclosure also may be directed to a substrate comprising a film on at least a portion thereof formed from a pretreatment composition disclosed herein. The substrate may comprise a film on at least a portion thereof formed from a pretreatment composition disclosed herein for example by making use of the system and/or method disclosed herein.

**[0081]** Suitable substrates that may be used include metal substrates, metal alloy substrates, substrates that have been metallized, such as nickel-plated plastic, and/or combinations thereof. The metal or metal alloy can comprise or be steel, aluminum, zinc, nickel, and/or magnesium. For example, the steel substrate could be cold rolled steel, hot rolled steel, electrogalvanized steel, and/or hot dipped galvanized steel. Aluminum alloys of the 1XXX, 2XXX, 3XXX, 4XXX, 5XXX, 6XXX, or 7XXX series as well as clad aluminum alloys also may be used as the substrate. Aluminum alloys may comprise, for example, 0.01% by weight copper to 10% by weight copper. Aluminum alloys which are treated may also include castings, such as 1XX.X, 2XX.X, 3XX.X, 4XX.X, 5XX.X, 6XX.X, 7XX.X, 8XX.X, or 9XX.X (e.g., A356.0). Magnesium alloys of the AZXX (including Eform Plus), AMXX, EVXX, ZKXX, ZEXX, ZCXX, HKXX, HZXX, QEXX, QHXX, WEXX, ZEK100, or Elektron 21 series also may be used as the substrate. The substrate used may also comprise titanium and/or titanium alloys, zinc

and/or zinc alloys, and/or nickel and/or nickel alloys. Suitable substrates for use in the present disclosure include those that are often used in the assembly of vehicle bodies (e.g., without limitation, door, body panel, trunk deck lid, roof panel, hood, roof and/or stringers, rivets, landing gear components, and/or skins used on an aircraft), a vehicular frame, vehicular parts, motorcycles, wheels, personal electronics, agricultural equipment, lawn and garden equipment, air conditioning units, heat pump units, lawn furniture, and other articles. As used herein, “vehicle” or variations thereof includes, but is not limited to, civilian, commercial and military aircraft, and/or land vehicles such as cars, automobiles, motorcycles, and/or trucks. The metal substrate also may be in the form of, for example, a sheet of metal or a fabricated part.

**[0082]** In examples, the substrate may comprise a three-dimensional component formed by an additive manufacturing process such as selective laser melting, e-beam melting, directed energy deposition, binder jetting, metal extrusion, and the like. In examples, the three-dimensional component may be a metal and/or resinous component.

**[0083]** As set forth above, the treated substrate may optionally further comprise a coating formed from a coating composition. The coating composition from which the coating is formed may comprise a film-forming resin. The coating composition may comprise an electrodepositable coating composition, a powder coating composition, and/or a liquid coating composition. The coating may be applied to at least a portion of the substrate by electrodeposition of the coating deposition, as described above.

**[0084]** The coated substrate of the present disclosure may for example comprise a topcoat. As used herein, the term “topcoat” refers to a mixture of binder(s) which can be an organic or inorganic based polymer or a blend of polymers, typically at least one pigment, can optionally contain at least one solvent or mixture of solvents, and can optionally contain at least one curing agent. A topcoat is typically the coating layer in a single or multi-layer coating system whose outer surface is exposed to the atmosphere or environment, and its inner surface is in contact with another coating layer or polymeric substrate. Examples of suitable topcoats include those conforming to MIL-PRF-85285D, such as those available from PPG (Defl 03W127A and Defl 03GY292). The topcoat may be an advanced performance topcoat, such as those available from PPG (Defthane<sup>®</sup> ELT<sup>™</sup>. 99GY001 and 99W009). However, other topcoats and advanced performance topcoats can be used as will be understood by those of skill in the art with reference to this disclosure.

**[0085]** The metal substrate also may comprise a self-priming topcoat, or an enhanced self-priming topcoat. The term “self-priming topcoat”, also referred to as “direct to substrate” or “direct to metal” coating, refers to a mixture of a binder(s), which can be an organic or inorganic based polymer or blend of polymers; typically, at least one pigment; can optionally contain at least one solvent or mixture of solvents; and can optionally contain at least one curing agent. The term “enhanced self-priming topcoat”, also referred to as an “enhanced direct to substrate coating”, refers to a mixture of functionalized fluorinated binders, such as a fluoroethylene-alkyl vinyl ether in whole or in part with other binder(s), which can be an organic or inorganic based polymer or blend of polymers, typically at least one pigment, can optionally contain at least one solvent or mixture of solvents, and can optionally contain at least one curing agent. Examples of self-priming topcoats include those available from PPG (03W169 and 03GY369), and examples of enhanced self-priming topcoats include Defthane<sup>®</sup> ELT<sup>™</sup>/ESPT and product code number 97GY121, available from PPG Industries Ohio, Inc. However, other self-priming topcoats and enhanced self-priming topcoats can be used in the coating system as will be understood by those of skill in the art with reference to this disclosure.

**[0086]** The self-priming topcoat and enhanced self-priming topcoat may be applied directly to the pretreated substrate. The self-priming topcoat and enhanced self-priming topcoat can optionally be applied to an organic or inorganic polymeric coating, such as a primer or paint film. The self-priming topcoat layer and enhanced self-priming topcoat is typically the coating layer in a single or multi-layer coating system where the outer surface of the coating is exposed to the atmosphere or environment, and the inner surface of the coating is typically in contact with the substrate or optional polymer coating or primer.

**[0087]** The topcoat, self-priming topcoat, and enhanced self-priming topcoat can be applied to the pretreated substrate, in either a wet or “not fully cured” condition that dries or cures over time, that is, solvent evaporates and/or there is a chemical reaction. The coatings can dry or cure either naturally or by accelerated means for example, an ultraviolet light cured system to form a film or “cured” paint.

**[0088]** In addition, a colorant and, if desired, various additives such as surfactants, wetting agents, or catalysts can be included in the coating composition (electrodepositable, powder, or liquid). As used herein, the term “colorant” means any substance that imparts color and/or other opacity and/or other visual effect to the composition. Example colorants include



pigments, dyes, and tints, such as those used in the paint industry and/or listed in the Dry Color Manufacturers Association (DCMA), as well as special effect compositions. In general, the colorant can be present in the coating composition in any amount sufficient to impart the desired visual and/or color effect. The colorant may comprise 1% to 65% by weight based on the total weight of the composition, such as 3% to 49% by weight, such as 5% to 35% by weight.

**[0089]** It has been surprisingly discovered that treatment of a substrate surface with a pretreatment composition comprising at least 25 ppm of a phosphonate based on total weight of the pretreatment composition, at 6 ppm of zinc based on total weight of the pretreatment composition and pH of no more than 6.0 results in significant improvement in corrosion resistance of metal substrates in comparison to compositions with only zinc, only a phosphonate, neither zinc nor a phosphonate, or a phosphonate at a lower concentration. As shown in the examples, the zinc provides improved corrosion resistance performance that is not shown by the addition of other metals, such as aluminum. Without intending to be limited by theory, it is believed that the zinc and phosphonate work synergistically to provide improved corrosion resistance. It has also been surprisingly discovered that corrosion resistance performance continues to improve as the concentrations of zinc and phosphonate increase up to high concentrations. It has also been surprisingly discovered that adding free fluoride to the pretreatment compositions disclosed herein further improves the corrosion resistance performance.

**[0090]** Whereas aspects of the disclosure have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular arrangements disclosed are meant to be illustrative only and not limited as to the scope of the disclosure which is to be given the full breadth of the claims and aspects appended and any and all equivalents thereof.

## EXAMPLES

### *Preparation of Cleaners and Pretreatment Compositions*

#### *Alkaline Cleaner*

**[0091]** An alkaline cleaner solution was prepared by adding 10 gallons of deionized water to a rectangular stainless-steel tank with a total volume of 37 gallons, equipped with spray nozzles. To this was added 500 mL of Chemklean 2010LP (a phosphate-free alkaline cleaner

available from PPG Industries, Inc.) and 50 mL of Chemkleen 181ALP (a phosphate-free blended surfactant additive available from PPG Industries, Inc.). The solution temperature was raised to 120°F.

**[0092]** A 10 mL sample of the alkaline cleaner was titrated with 0.100 N sulfuric acid to measure the free and total alkalinity. The free alkalinity was 5.2 mL as measured using a phenolphthalein end point (pink to colorless color change) and the total alkalinity was 6.4 mL as measured to a bromocresol green end point (blue to yellow color change).

#### *Pretreatment Compositions*

**[0093]** Fourteen different pretreatment compositions (PT 1-14) were prepared for testing. The compositions are listed in Table 1, below. Zinc was supplied by adding zinc oxide, available from Fisher Scientific (Fair Lawn, NJ); etidronic acid was supplied by adding hydroxyl ethylidene (1, 1-diphosphonic acid) (58 wt%), available from Italmatch (Manchester, UK) for pretreatments 1-3, 6-8, and 10 and hydroxyl ethylidene (1, 1-diphosphonic acid) (58 wt%), available from PPG Industries, Inc. (Euclid, OH) for pretreatments 4, 5, 9, and 11-14; aluminum was supplied by adding aluminum chloride, available from Fisher Scientific (Fair Lawn, NJ); free fluoride was supplied by adding potassium bifluoride (99.3%), available from Sigma-Aldrich (St. Louis, MO); and zirconium was supplied by adding fluorozirconic acid (45 wt.% in water) available from Honeywell International, Inc. (Morristown, NJ).

**[0094]** All of the compositions, as detailed below, were prepared in DI water and maintained at 75°F with an immersion heater (Polyscience Sous Vide Professional, Model # 7306AC1B5, available from Polyscience, Niles, Illinois). Baths containing pretreatment were set to low agitation mode during immersion of panels to circulate and heat the composition contained therein.

**[0095]** After all of the ingredients were added to the pretreatment bath, pH was measured using a pH meter (interface, DualStar pH/ISE Dual Channel Benchtop Meter, available from ThermoFisher Scientific, Waltham, Massachusetts, USA; pH probe, Fisher Scientific Accumet pH probe (Ag/AgCl reference electrode)) by immersing the pH probe in the pretreatment solution. Free fluoride was measured using a DualStar pH/ISE Dual Channel Benchtop Meter (ThermoFisher Scientific) equipped with a fluoride selective electrode (Orion ISE Fluoride Electrode, solid state, available from ThermoFisher Scientific) by immersing the ISE in the pretreatment solution and allowing the measurement to equilibrate. Then, the pH was adjusted

as needed with Chemfil buffer (an alkaline buffering solution, commercially available from PPG Industries, Inc.). The free fluoride was adjusted as needed with Chemfos AFL (a partially neutralized aqueous ammonium bifluoride solution, commercially available from PPG Industries, Inc and prepared according to supplier instructions).

(i) Pretreatment Composition Bath 1 (PT 1)

**[0096]** To a clean two-gallon plastic bucket were added 32.99 g of zinc oxide, 167 g of etidronic acid, and 3.65 liters of deionized water. The pH and free fluoride were measured as described above and pH was adjusted with Chemfil buffer. The pH and free fluoride were adjusted to the values recorded in Table 1.

(ii) Pretreatment Composition Bath 2 (PT 2) (Comparative)

**[0097]** To a clean 64-ounce plastic container were added 30 g of etidronic acid and 0.57 liters of deionized water. The pH was measured as described above and the results recorded in Table 1.

(iii) Pretreatment Composition Bath 3 (PT 3) (Comparative)

**[0098]** To a clean 64-ounce plastic container were added 52.92 g of aluminum etidronate derivative and 0.547 liters of deionized water. The pH was measured as described above and the results recorded in Table 1.

**[0099]** Aluminum etidronate derivative was prepared by adding 13.36 g of anhydrous aluminum chloride portion-wise to a 58 wt% solution of etidronic acid in a clean 500 mL round bottom flask. The reaction vigorously exothermed upon addition of the aluminum salt. A charge of 15.28 g of deionized water was then added to the reaction and the resultant mixture was stirred at room temperature for approximately 43 hours using a Thermolyne Nuova SP18425 stir plate and a magnetic stir bar. The volatiles were then removed under reduced pressure on a BUCHI RE-111 rotary evaporator for 4 hours. The remaining viscous liquid was dissolved in deionized water to produce the aluminum etidronate derivative at 56.69% total solids.

(iv) Pretreatment Composition Bath 4 (PT 4) (Comparative)

**[0100]** To a clean two-gallon plastic bucket were added 10.70 mg of zinc oxide, 50.20 mg of etidronic acid, and 3.95 liters of deionized water. The pH was measured as described above and the results recorded in Table 1.

(v) Pretreatment Composition Bath 5 (PT 5)

**[0101]** To a clean two-gallon plastic bucket were added 32.99 g of zinc oxide, 167 g of etidronic acid, and 3.8 liters of deionized water. The pH and free fluoride were measured as described above. The pH was adjusted with Chemfil buffer, and the free fluoride was adjusted with Chemfos AFL to the values recorded in Table 1.

(vi) Pretreatment Composition Bath 6 (PT 6)

**[0102]** To a clean two-gallon plastic bucket were added 32.99 mg of zinc oxide, 167 mg of etidronic acid, and 3.9 liters of deionized water. The pH and free fluoride were measured as described above. The pH was adjusted with Chemfil buffer, and the free fluoride was adjusted with Chemfos AFL to the values recorded in Table 1.

(vii) Pretreatment Composition Bath 7 (PT 7) (Comparative)

**[0103]** To a clean one-gallon plastic bucket were added 17.75 g of zinc oxide and 1.58 liters of deionized water.

(viii) Pretreatment Composition Bath 8 (PT 8) (Comparative)

**[0104]** To a clean three-gallon plastic bucket was added 11.25 liters of deionized water. Fluorozirconic acid (80.13 g), potassium bifluoride (7 g) and sodium hydroxide (9.5 g) were then added. The pH and free fluoride were measured as described above and results were recorded in Table 1.

(ix) Pretreatment Composition Bath 9 (PT 9)

**[0105]** To a clean two-gallon plastic bucket were added 10.99 g of zinc oxide, 167 g of etidronic acid, and 3.8 liters of deionized water. The pH and free fluoride were measured as described above. The pH was adjusted with Chemfil buffer, and the free fluoride was adjusted with Chemfos AFL to the values recorded in Table 1.

(x) Pretreatment Composition Bath 10 (PT 10)

**[0106]** To a clean two-gallon plastic bucket were added 32.99 g of zinc oxide, 167 g of etidronic acid, and 3.8 liters of deionized water. The pH was measured as described above and adjusted with Chemfil buffer to the value recorded in Table 1.

(xi) Pretreatment Composition Bath 11 (PT 11) (Comparative)

**[0107]** To a clean one-gallon bucket were added 60.01 g of etidronic acid and 1.58 liters of deionized water. The pH and free fluoride were measured as described above and the results recorded in Table 1.

(xii) Pretreatment Composition Bath 12 (PT 12) (Comparative)

**[0108]** To a clean two-gallon plastic bucket were added 3.1 mg of zinc oxide, 61 mg of etidronic acid, and 3.95 liters of deionized water. The pH and free fluoride were measured as described above and the results recorded in Table 1.

(xiii) Pretreatment Composition Bath 13 (PT 13) (Comparative)

**[0109]** To a clean one-gallon plastic bucket were added 17.75 g of zinc oxide and 1.58 liters of deionized water. The pH and free fluoride were measured as described above and the results recorded in Table 1.

(xiv) Pretreatment Composition Bath 14 (PT 14)

**[0110]** To a clean one-gallon plastic bucket were added 16.55 g of zinc oxide, 83.50 g of etidronic acid, and 1.8 liters of deionized water. The pH and free fluoride were measured as described above and the results recorded in Table 1.

Table 1. Pretreatment Compositions Prior to Use

Code	Etidronic acid (ppm)	Zn (ppm)	Al (ppm)	pH	Free fluoride (ppm)
PT 1	4,573	7,262	-	2.31	214
PT 2*	52,632	-	-	1.14	-
PT 3*	33,000	-	16,000	0.90	-
PT 4*	12.71	3.46	-	4.00	-
PT 5	43,947	6,975	-	3.11	274
PT 6	42.82	6.80	-	3.51	531
PT 7*	-	9,026	-	-	-
PT 8*	-	-	-	2.37	72
PT 9	43,947	2,324	-	2.94	274
PT 10	43,947	6,975	-	2.01	-
PT 11*	37,981	-	-	1.80	-
PT 12*	15.44	0.63	-	3.72	-
PT 13*	-	9,026	-	7.40	-
PT 14	46,389	7,387	-	2.08	-

\*Comparative Example

**[0111]** For Examples 1-4, AZ21 magnesium alloy (known commercially as “Eform Plus” or abbreviated “EFP”) supplied by USAMP from POSCO (Pohang, SK) was evaluated. Substrates were cut to 4” by 6” using a panel cutter prior to application of the alkaline cleaner.

**[0112]** Panels were treated using either Treatment Method A or B, outlined in Tables 2 and 3, respectively, below. For panels treated according to Treatment Method A, panels were spray cleaned and degreased for 120 seconds at 10-15 psi in the alkaline cleaner (120°F) using

Vee-jet nozzles and rinsed with deionized water by immersing in a deionized water bath (75°F) for 30 seconds followed by a deionized water spray rinse using a Melnor Rear-Trigger 7-Pattern nozzle set to shower mode (available from Home Depot). All panels were immersed in one of PT 1 through PT 10 for 120 seconds (75°F), rinsed by a deionized water spray rinse using a Melnor Rear-Trigger 7-Pattern nozzle set to shower mode (75°F) for 30 seconds, and dried with hot air (140°F) for 120 seconds using a Hi-Velocity handheld blow dryer made by Oster® (model number 078302-300-000) on high setting.

**[0113]** For panels treated according to Treatment Method B, panels were spray cleaned and degreased for 120 seconds at 10-15 psi in the alkaline cleaner (120°F) using Vee-jet nozzles and rinsed with deionized water by immersing in a deionized water bath (75°F) for 30 seconds followed by a deionized water spray rinse using a Melnor Rear-Trigger 7-Pattern nozzle set to shower mode (available from Home Depot). All panels were dried with hot air (140°F) for 120 seconds using a Hi-Velocity handheld blow dryer made by Oster® (model number 078302-300-000) on high setting.

Table 2. Treatment Method A

Step 1A	Alkaline cleaner (120 seconds, 120°F, spray application)
Step 2A	Deionized water rinse (30 seconds, 75°F, immersion application)
Step 3A	Deionized water rinse (30 seconds, 75°F, spray application)
Step 4A	Pretreatment (120 seconds, 75°F, immersion application)
Step 5A	Deionized water rinse (30 seconds, 75°F, spray application)
Step 6A	Hot Air Dry (120 seconds, 140°F)

Table 3. Treatment Method B

Step 1B	Alkaline cleaner (120 seconds, 120°F, spray application)
Step 2B	Deionized water rinse (30 seconds, 75°F, immersion application)
Step 3B	Deionized water rinse (30 seconds, 75°F, spray application)
Step 4B	Hot Air Dry (120 seconds, 140°F)

**[0114]** In all Examples, following completion of Treatment Method A or B, all panels were treated with EPIC 200 (a cationic electrocoat with components commercially available from PPG and prepared in accordance with manufacturer’s instructions). In all cases, the electrocoat paint was ultrafiltered removing 25% of the material, which was replenished with fresh deionized water. The rectifier (Xantrax Model XFR600-2, Elkhart, Indiana, or Sorensen XG 300-5 6, Ametec, Berwyn, Pennsylvania) was DC power supplied. The electrocoat application conditions were a voltage set point of 170V-180V, a ramp time of 30s, and a current

density of 1.6 mA/cm<sup>2</sup>. The electrocoat composition was maintained at 92°F using a heating coil. The film thickness was coulomb controlled to deposit a target film thickness of 0.75 ± 0.2 mils for EPIC. The DFT was controlled by changing the amount of charge (coulombs) that passed through the panels. Following deposition of the electrocoat, panels were baked in an oven (Despatch Model LFD-1- 42) at 177°C for 25 minutes.

**[0115]** Electrocoated panels were vertically or X-scribed on one side of the panel down to the metal substrate. For corrosion performance evaluation, EFP panels were placed in ASTM G85 A2 testing for a minimum of 3 weeks (i.e., 21 cycles). After the exposure, corroded panels were dried under ambient conditions until dry to the touch. For EFP panels, the loose coating around the scribe was removed by applying a scotch filament tape (3M Industries Adhesives and Tapes Divisions, St. Paul, MN) and pulling it off. Afterwards, the width of exposed metal region along the scribe was recorded for 5-12 locations and averaged to assess the corrosion performance of the panel. As used herein, scribe creep refers to the area of paint loss around the scribe either through corrosion or disbondment (e.g., effected paint to effected paint). Panels for PT 2 and PT 3 were run in duplicate, panels for PT 4, PT 5, and PT 9 were run in quadruplicates, and panels for PT 1, PT 6, PT 7, PT 8, and PT 10 were run in octuplicates.

**[0116]** Elemental testing was performed using X-Ray Fluorescence spectroscopy (XRF), XPS depth profiling, and FIB/TEM/EDX. (XRF testing was performed using X-Met 7500, Oxford Instruments; operating parameters for phosphorus: 60 second timed assay, 15 Kv, 45 μA, K $\alpha$ , T(p) = 1.1 s<sup>-1</sup> (reported as P counts below)); operating parameters for zinc: 60 second timed assay, 25 Kv, 20 μA, K $\alpha$ , T(p) = 1.1 s<sup>-1</sup> (reported as Zn counts).

**[0117]** XPS depth profiling was performed using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al k<sup>α</sup> x-ray source (h $\nu$  = 1,486.7 eV) and a concentric hemispherical analyzer.

**[0118]** FIB/TEM/EDX was performed using a FEI Helios NanoLab 660. To prepare a cross-section of the panel for TEM analysis, a protective layer of carbon and a protective layer of gold was deposited on the sample before the focused ion beam (FIB) preparation. The focused ion beam (FIB) lift-out method was used. High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) and energy dispersive x-ray spectroscopy (EDX) analysis was performed at Penn State University's Materials Research Institute on the FEI Talos TEM (200kV).

**Example 1**

**Corrosion performance on AZ21 panels treated with alkaline cleaner and PT 1, PT 2, PT 3, or PT 7**

[0119] AZ21 panels were treated according to Treatment Method A (Table 2). Panels were then electrocoated with EPIC 200 according to the parameters described above. Panels were scribed and subjected to G-85 cyclic corrosion testing as specified in Table 4.

Table 4. Average G-85 scribe creep results for Example 1

<b>Pretreatment Code</b>	<b>AZ21 scribe creep (42 cycles, mm)</b>	<b>AZ21 scribe creep (21 cycles, mm)</b>	<b>AZ21 scribe creep (mm/cycle)</b>
PT 1	1.43	-	0.034
PT 2	-	15.71	0.748
PT 3	-	53.42	2.54
PT 7	-	18.22	0.868

[0120] This example shows that AZ21 panels treated with PT 1 had better corrosion performance in comparison to panels treated with PT 2, PT 3, or PT 7 as demonstrated by an average scribe creep of 1.43 mm following exposure to 42 cycles of G-85 cyclic corrosion testing and an average scribe creep of 0.034 mm/cycle of G-85 cyclic corrosion testing. PT 2, PT 3, and PT 7 were not extended to 42 cycles because their corrosion performance at 21 cycles was so poor that 42 cycles would likely result in extensive corrosion that could not be measured or differentiated from the other pretreatments in the same set.

**Example 2**

**Corrosion performance on AZ21 panels treated with alkaline cleaner with and without PT 1 or PT 8**

[0121] AZ21 panels were treated according to either Treatment Method A or B (Table 2 and 3). Panels were then electrocoated with EPIC 200 according to the parameters described above. Panels were scribed and subjected to G-85 cyclic corrosion testing as specified in Table 5.

Table 5. Average G-85 scribe creep results for Example 2

<b>Treatment Method</b>	<b>Pretreatment Code</b>	<b>AZ21 scribe creep (42 cycles, mm)</b>	<b>AZ21 scribe creep (21 cycles, mm)</b>	<b>AZ21 scribe creep (mm/cycle)</b>
A	PT 1	1.43	-	0.034
A	PT 8	2.49	-	0.059
B	-	-	18.68	0.890

[0122] This example shows that AZ21 panels treated with PT 1 have comparably better corrosion performance to PT 8 on AZ21 and performs considerably better than the alkaline clean



only comparative control, or Treatment Method B, as demonstrated by an average scribe creep of 1.43 mm following exposure to 42 cycles of salt spray testing and an average scribe creep of 0.034 mm/cycle of salt spray testing. Treatment Method B was not run to 42 cycles because the corrosion performance was so poor that 42 cycles would likely show result in extensive corrosion that could not be measured or differentiated from the other pretreatments in the same set.

**Example 3**

**Corrosion performance on AZ21 panels treated with alkaline cleaner and PT 1, PT 4, PT 5, or PT 6**

[0123] AZ21 panels were treated according to Treatment Method A (Table 2). Panels were then electrocoated with EPIC 200 according to the parameters described above. Panels were scribed and subjected to G-85 cyclic corrosion testing as specified in Table 6.

Table 6. Average G-85 scribe creep results for Example 3

<b>Pretreatment Code</b>	<b>AZ21 scribe creep (42 cycles, mm)</b>	<b>AZ21 scribe creep (mm/cycle)</b>
PT 1	1.43	0.034
PT 4	13.86	0.330
PT 5	4.44	0.106
PT 6	8.59	0.205
PT 9	3.02	0.072

[0124] This example shows that AZ21 panels treated with PT 1 had better corrosion performance than AZ21 panels treated with PT 4, PT 5, PT 6, or PT 9 as demonstrated by an average scribe creep of 1.43 mm following exposure to 42 cycles of salt spray testing and an average scribe creep of 0.034 mm/cycle of salt spray testing. This example also shows that AZ21 panels treated with PT 5, PT 6, and PT 9, which demonstrate different operating ranges of zinc and etidronic acid, give noticeably better corrosion performance on AZ21 in comparison to PT 4. This is demonstrated by an average scribe creep after 42 cycles of G-85 corrosion testing of 4.44 mm, 8.59 mm, and 3.02 mm for PT 5, PT 6, and PT 9, respectively, versus an average scribe creep of 13.86 mm for PT 4.

**Example 4**

**Corrosion performance on AZ21 panels treated with alkaline cleaner and PT 1 or PT 10**

[0125] AZ21 panels were treated according to Treatment Method A (Table 2). Panels were then electrocoated with EPIC 200 according to the parameters described above. Panels were scribed and subjected to G-85 cyclic corrosion testing as specified in Table 7.

Table 7. Average G-85 scribe creep results for Example 4

Pretreatment Code	AZ21 scribe creep (42 cycles, mm)	AZ21 scribe creep (mm/cycle)
PT 5	4.44	0.106
PT 10	8.81	0.210

[0126] This example shows that AZ21 panels treated with PT 5, containing 274 ppm of free fluoride, had better corrosion performance than AZ21 panels treated with PT 10, containing no free fluoride. Panels treated with PT 5 exhibited an average scribe creep of 4.44 mm after exposure to 42 cycles of G-85 cyclic corrosion testing. By comparison, panels treated with PT 10 exhibited an average scribe creep of 8.81 mm after exposure to the same testing. Thus, the addition of free fluoride to PT 5 provided superior corrosion performance.

**Example 5**  
**pH and free fluoride measured for PT 11, PT 12, PT 13, and PT 14**

[0127] PT 11, PT 12, PT 13, and PT 14 were prepared as described above. The pH and free fluoride of each pretreatment were measured as described above and recorded in Table 8. This example confirms the pH and free fluoride ranges for PT 2, PT 4, PT 7, and PT 10.

Table 8. pH and free fluoride measurement results for Example 6

Pretreatment Code	pH	Free Fluoride (ppm)
PT 11	1.80	0.00034
PT 12	3.72	0.0033
PT 13	7.40	0.10
PT 14	2.08	0.00099

We claim:

1. A pretreatment composition comprising:  
at least 25 ppm of a phosphonate based on total weight of the pretreatment composition;  
at least 6 ppm of zinc based on total weight of the pretreatment composition; and  
a pH of 6.0 or less.
2. The pretreatment composition of claim 1, wherein the pretreatment composition comprises at least 30 ppm, or at least 40 ppm, or at least 500 ppm, or at least 2,000 ppm, or at least 4,000 ppm of the phosphonate based on total weight of the pretreatment composition; and/or no more than 60,000 ppm, or no more than 55,000 ppm, or no more than 50,000 ppm of the phosphonate based on total weight of the pretreatment composition.
3. The pretreatment composition of claim 1 or claim 2, wherein the pretreatment composition comprises 25 ppm to 60,000 ppm, or 30 ppm to 55,000 ppm, or 40 ppm to 50,000 ppm, or 500 ppm to 55,000 ppm, or 2,000 ppm to 55,000 ppm, or 4,000 ppm to 55,000 ppm, or 500 ppm to 50,000 ppm, or 2,000 ppm to 50,000 ppm, or 4,000 ppm to 50,000 ppm of the phosphonate, based on total weight of the pretreatment composition.
4. The pretreatment composition of any of the preceding claims, wherein the pretreatment composition further comprises free fluoride.
5. The pretreatment composition of claim 4, wherein the pretreatment composition comprises at least 15 ppm, or at least 50 ppm, or at least 100 ppm, or at least 150 ppm, or at least 200 ppm, of free fluoride based on total weight of the pretreatment composition; and/or no more than 750 ppm, or no more than 700 ppm, or no more than 650 ppm, or no more than 600 ppm, or no more than 550 ppm, of free fluoride based on total weight of the pretreatment composition.
6. The pretreatment composition of claim 4 or claim 5, wherein the pretreatment composition comprises 15 ppm to 750 ppm, or 50 ppm to 700 ppm, or 100 ppm to 650 ppm, or

150 ppm to 600 ppm, or 200 ppm to 550 ppm of the free fluoride based on total weight of the pretreatment composition.

7. The pretreatment composition of any of the preceding claims, wherein the phosphonate comprises a phosphonic acid.

8. The pretreatment composition of claim 7, wherein the phosphonic acid comprises a monophosphonic acid, a diphosphonic acid, and/or a polyphosphonic acid.

9. The pretreatment composition of claim 8, wherein the diphosphonic acid comprises etidronic acid or a derivative thereof.

10. The pretreatment composition of any of the preceding claims, wherein the pretreatment composition comprises at least 6 ppm, or at least 100 ppm, or at least 500 ppm, or at least 1,000 ppm, or at least 1,500 ppm, and/or no more than 15,000 ppm, or no more than 12,000 ppm, or no more than 10,000 ppm, or no more than 7,500 ppm of zinc based on total weight of the pretreatment composition.

11. The pretreatment composition of any of the preceding claims, wherein the pretreatment composition comprises 6 ppm to 15,000 ppm, or 100 ppm to 15,000 ppm, or 100 ppm to 12,000 ppm, or 100 ppm to 10,000 ppm, or 100 ppm to 7,500 ppm, or 500 ppm to 12,000 ppm, or 500 ppm to 10,000 ppm, or 750 ppm to 7,500 ppm, or 1,000 ppm to 10,000 ppm, or 1,500 ppm to 7,500 ppm of the zinc, based on total weight of the pretreatment composition.

12. The pretreatment composition of any of the preceding claims, wherein the zinc comprises a salt, a compound, or combinations thereof.

13. The pretreatment composition of any of the preceding claims, wherein the pretreatment composition comprises a pH of 6.0 or less, or 5.0 or less, or 4.0 or less, and/or a pH of at least 0.3, or at least 0.5, or at least 0.8, or at least 0.9, or at least 1.0, or at least 1.5, or at least 2.0.

14. The pretreatment composition of any of the preceding claims, wherein the pretreatment composition comprises a pH of 0.3 to 6.0, or 0.3 to 5.0, or 0.3 to 4.0, or 0.5 to 6.0, or 0.5 to 5.0, or 0.5 to 4.0, or 0.8 to 6.0, or 0.8 to 5.0, or 0.8 to 4.0, or 1.0 to 6.0, or 1.0 to 5.0, or 1.0 to 4.0, or 1.5 to 4.0, or 2.0 to 4.0.
15. The pretreatment composition of any of the preceding claims, wherein the pretreatment composition is substantially free of chromium and/or organic compounds other than phosphonates or phosphonic acids.
16. The pretreatment composition of any of the preceding claims, wherein the pretreatment composition comprises an aqueous medium.
17. A system for treating a substrate comprising:  
a cleaning composition; and  
the pretreatment composition of any of the preceding claims.
18. The system of claim 17, wherein the cleaning composition comprises an alkaline pH.
19. The system of claim 17 or claim 18, wherein the cleaning composition comprises a pH of at least 10.0, or at least 10.5.
20. The system of any of claims 17 to 19, further comprising a coating composition comprising a film-forming resin.
21. The system of claim 20, wherein the coating composition comprises an electrodepositable coating composition, a powder coating composition, and/or a liquid coating composition.
22. A method of treating a substrate comprising contacting at least a portion of the substrate surface with the pretreatment composition of any of claims 1 to 16.

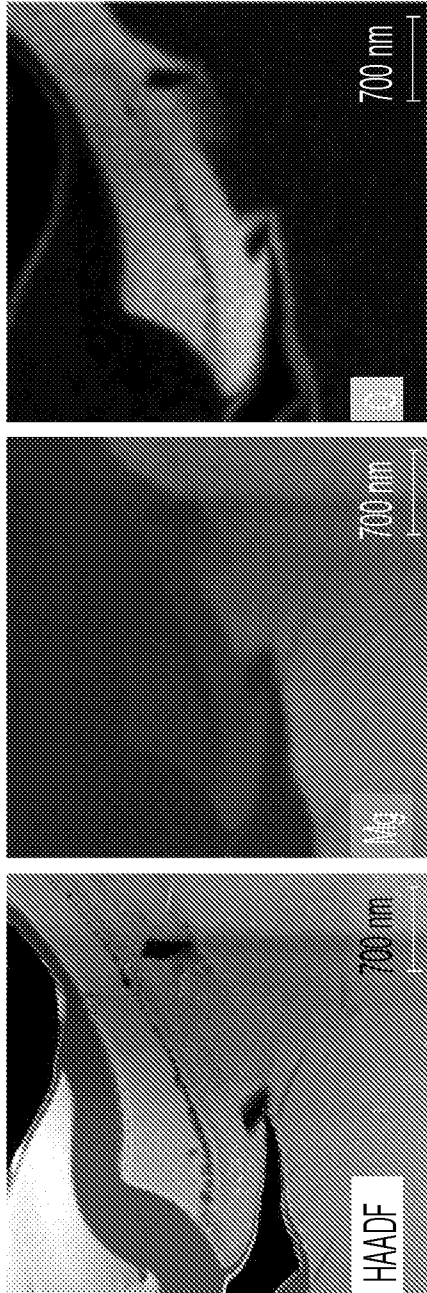
23. The method of claim 22, further comprising contacting at least a portion of the substrate surface with a cleaning composition prior to the contacting with the pretreatment composition.
24. The method of claim 23, wherein the cleaning composition comprises an alkaline pH.
25. The method of any of claims 22 to 24, further comprising contacting at least a portion of the substrate with a coating composition comprising a film-forming resin following the contacting with the pretreatment composition.
26. A substrate treated with the pretreatment composition of any of claims 1 to 16.
27. A substrate treated with the system of any of claims 17 to 21.
28. A substrate treated with the method of any of claims 22 to 25.
29. The substrate of any of claims 26 to 28, wherein the substrate comprises a metal and/or a metal alloy.
30. The substrate of any of claims 26 to 29, wherein the substrate comprises magnesium, magnesium alloy, or combinations thereof.
31. The substrate of any of claims 26 to 30, wherein the substrate comprises a vehicle, personal electronic device, a part, an article, components thereof, or combinations thereof.
32. The substrate of any of claims 26 to 31, wherein the substrate comprises a three-dimensional component formed by an additive manufacturing process.
33. The substrate of claim 32, wherein the additive manufacturing process comprises selective laser melting, e-beam melting, directed energy deposition, metal extrusion, and/or binder jetting.

34. The substrate of any of claims 26 to 33, wherein the substrate is treated with a coating composition.

35. The substrate of claim 34, wherein the coating composition comprises a film-forming resin.

36. The substrate of claim 34 or claim 35, wherein the coating composition comprises an electrodepositable coating composition, powder coating composition, and/or a liquid coating composition.

FIG. 1

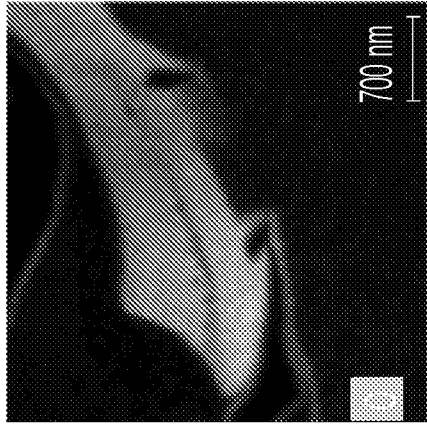


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1A

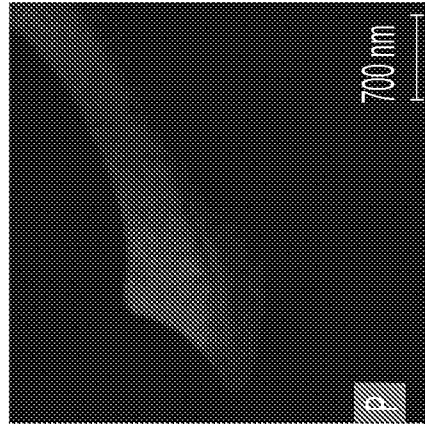
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1B



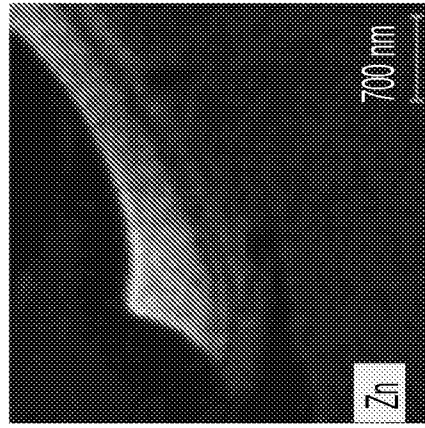
MAG: 28.5kx HV: 200kV

1C



MAG: 28.5kx HV: 200kV

1D



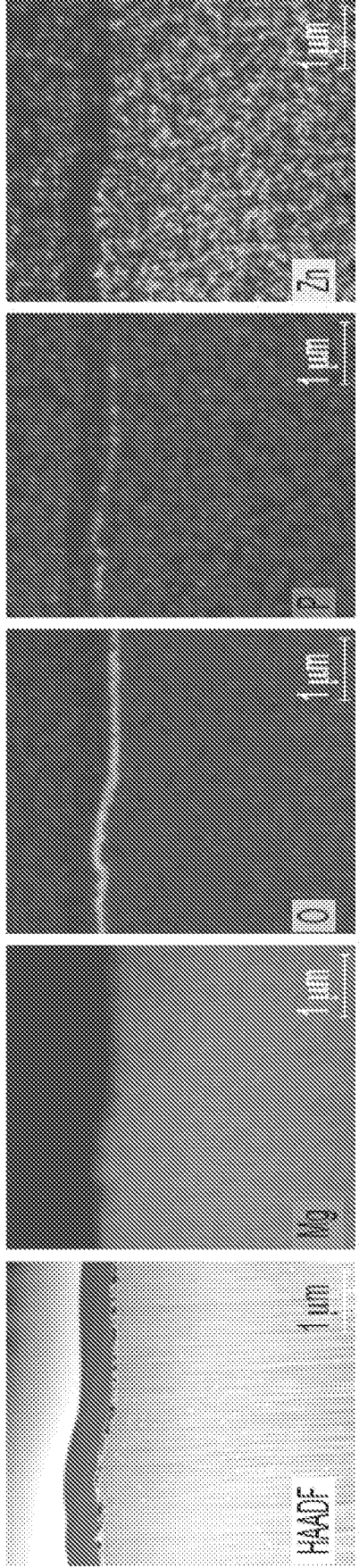
MAG: 28.5kx HV: 200kV

1E



FIG. 2

(Treatment Method B) - Alkaline Clean



HAADF  
MAG: 20.0kx HV: 200kV

Mg  
MAG: 20.0kx HV: 200kV

O  
MAG: 20.0kx HV: 200kV

P  
MAG: 20.0kx HV: 200kV

Zn  
MAG: 20.0kx HV: 200kV

2A

2B

2C

2D

2E

FIG. 3

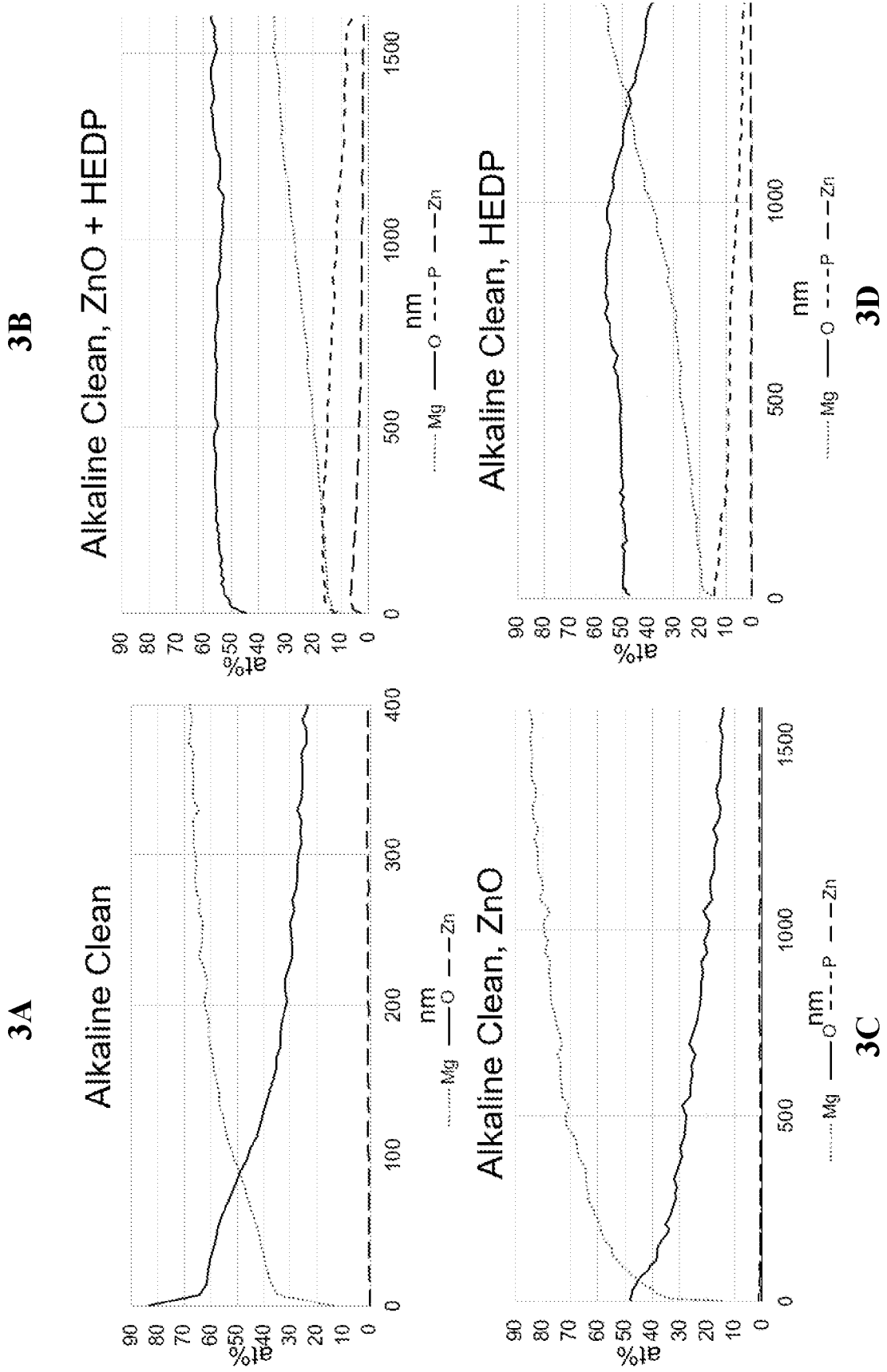
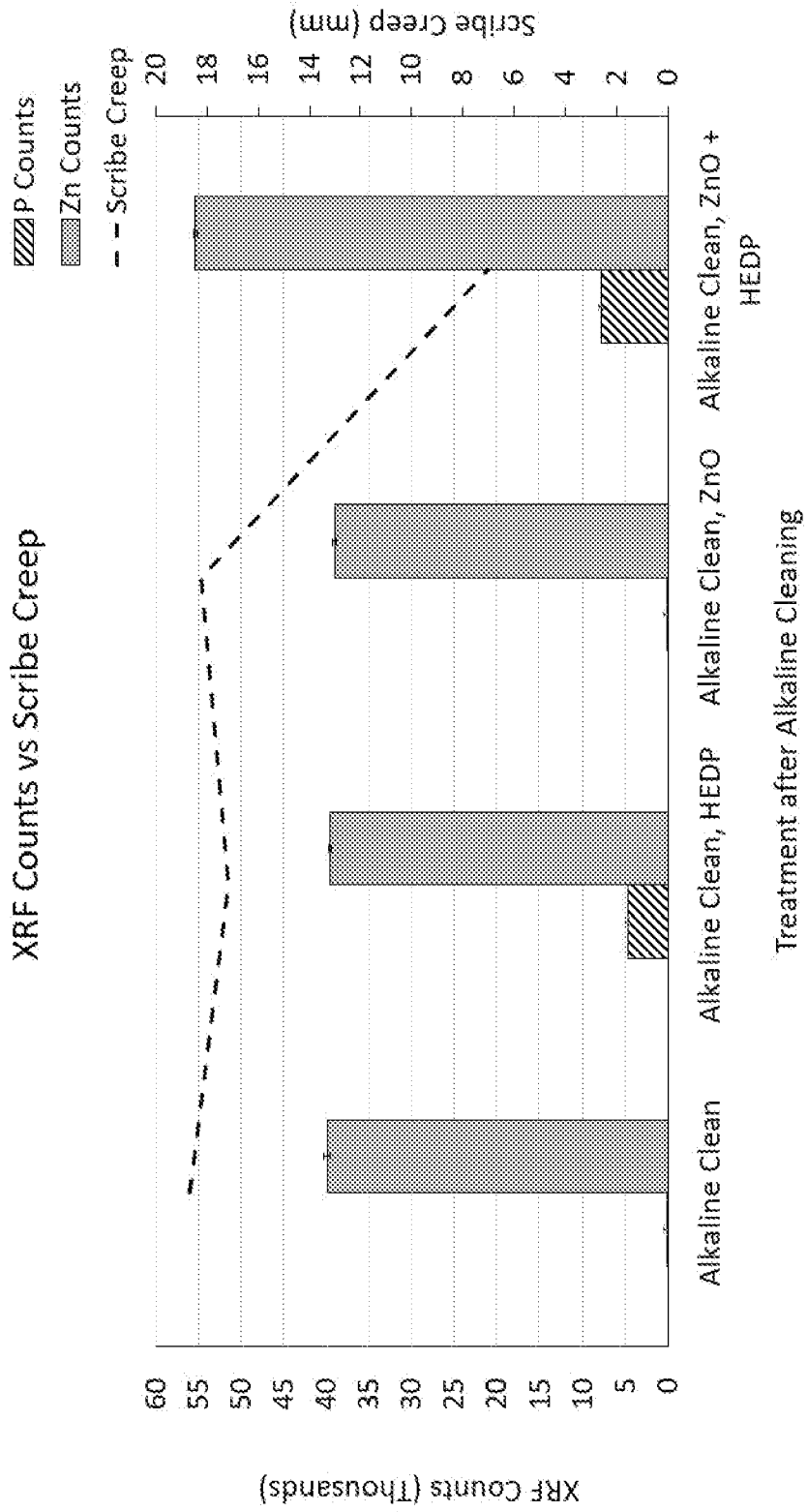


FIG. 4



**INTERNATIONAL SEARCH REPORT**

International application No  
**PCT/US2022/077333**

**A. CLASSIFICATION OF SUBJECT MATTER**  
**INV. C23C22/12 C23C22/20 C23C22/36 C23C22/68 C23C22/78**  
**ADD.**

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

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
**C23C**

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
**EPO-Internal, WPI Data**

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<b>X</b>	<b>US 2011/008645 A1 (SCHNEIDER MARK ANDRE [DE] ET AL) 13 January 2011 (2011-01-13)</b>  <b>paragraphs [0030], [0035]</b> <b>paragraph [0104] - paragraph [0107]</b> <b>examples E1-E10, E12-E20; table 1</b> -----	<b>1-19,</b> <b>22-24,</b> <b>26-34</b>
<b>X</b>	<b>WO 02/24975 A1 (HENKEL CORP [US]; MEAGHER KEVIN K [US]) 28 March 2002 (2002-03-28)</b>	<b>1-4,</b> <b>7-18,</b> <b>20-29,</b> <b>31, 34-36</b>
<b>A</b>	<b>table 1</b> <b>point (E);</b> <b>page 5</b> <b>bottom;</b> <b>page 12 - page 13</b> -----	<b>5, 6, 19,</b> <b>30, 32, 33</b>

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  <b>4 January 2023</b>	Date of mailing of the international search report  <b>13/01/2023</b>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  <b>Fodor, Anna</b>
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

**PCT/US2022/077333**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
<b>US 2011008645</b>	<b>A1</b>	<b>13-01-2011</b>	<b>AU 2009224757 A1</b>	<b>17-09-2009</b>
			<b>CA 2718242 A1</b>	<b>17-09-2009</b>
			<b>CN 102027157 A</b>	<b>20-04-2011</b>
			<b>DE 102008000600 A1</b>	<b>17-09-2009</b>
			<b>EP 2255025 A1</b>	<b>01-12-2010</b>
			<b>ES 2547119 T3</b>	<b>01-10-2015</b>
			<b>JP 5562261 B2</b>	<b>30-07-2014</b>
			<b>JP 2011517727 A</b>	<b>16-06-2011</b>
			<b>PL 2255025 T3</b>	<b>30-11-2015</b>
			<b>US 2011008645 A1</b>	<b>13-01-2011</b>
			<b>US 2017314137 A1</b>	<b>02-11-2017</b>
			<b>WO 2009112480 A1</b>	<b>17-09-2009</b>
			<b>ZA 201007246 B</b>	<b>25-01-2012</b>
			-----	
<b>WO 0224975</b>	<b>A1</b>	<b>28-03-2002</b>	<b>AU 9468601 A</b>	<b>02-04-2002</b>
			<b>CA 2423059 A1</b>	<b>28-03-2002</b>
			<b>EP 1325172 A1</b>	<b>09-07-2003</b>
			<b>JP 2004515646 A</b>	<b>27-05-2004</b>
			<b>KR 20030046461 A</b>	<b>12-06-2003</b>
			<b>MX PA03002397 A</b>	<b>10-09-2004</b>
			<b>US 2003188807 A1</b>	<b>09-10-2003</b>
			<b>WO 0224975 A1</b>	<b>28-03-2002</b>
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