US 20240076781A1

(19) **United States**

(12) **Patent Application Publication**

Allen et al.

(10) **Pub. No.: US 2024/0076781 A1**

(43) **Pub. Date: Mar. 7, 2024**

(54) **SYSTEMS AND METHODS FOR TREATING A METAL SUBSTRATE**

(71) Applicant: **PPG Industries Ohio, Inc.**, Cleveland, OH (US)

(72) Inventors: **Kristi M. Allen**, Pittsburgh, PA (US); **Rachel D. Harris**, Pittsburgh, PA (US); **Justin J. Martin**, Harrison City, PA (US); **Steven J. Lemon**, Lower Burrell, PA (US); **Silvia Bezer**, Gibsonia, PA (US); **Mark W. McMillen**, Cabot, PA (US)

(73) Assignee: **PPG Industries Ohio, Inc.**, Cleveland, OH (US)

(21) Appl. No.: **17/754,568**

(22) PCT Filed: **Aug. 10, 2020**

(86) PCT No.: **PCT/US2020/045656**

§ 371 (c)(1),
(2) Date: **Apr. 6, 2022**

Related U.S. Application Data

(60) Provisional application No. 62/913,482, filed on Oct. 10, 2019, provisional application No. 62/913,500, filed on Oct. 10, 2019.

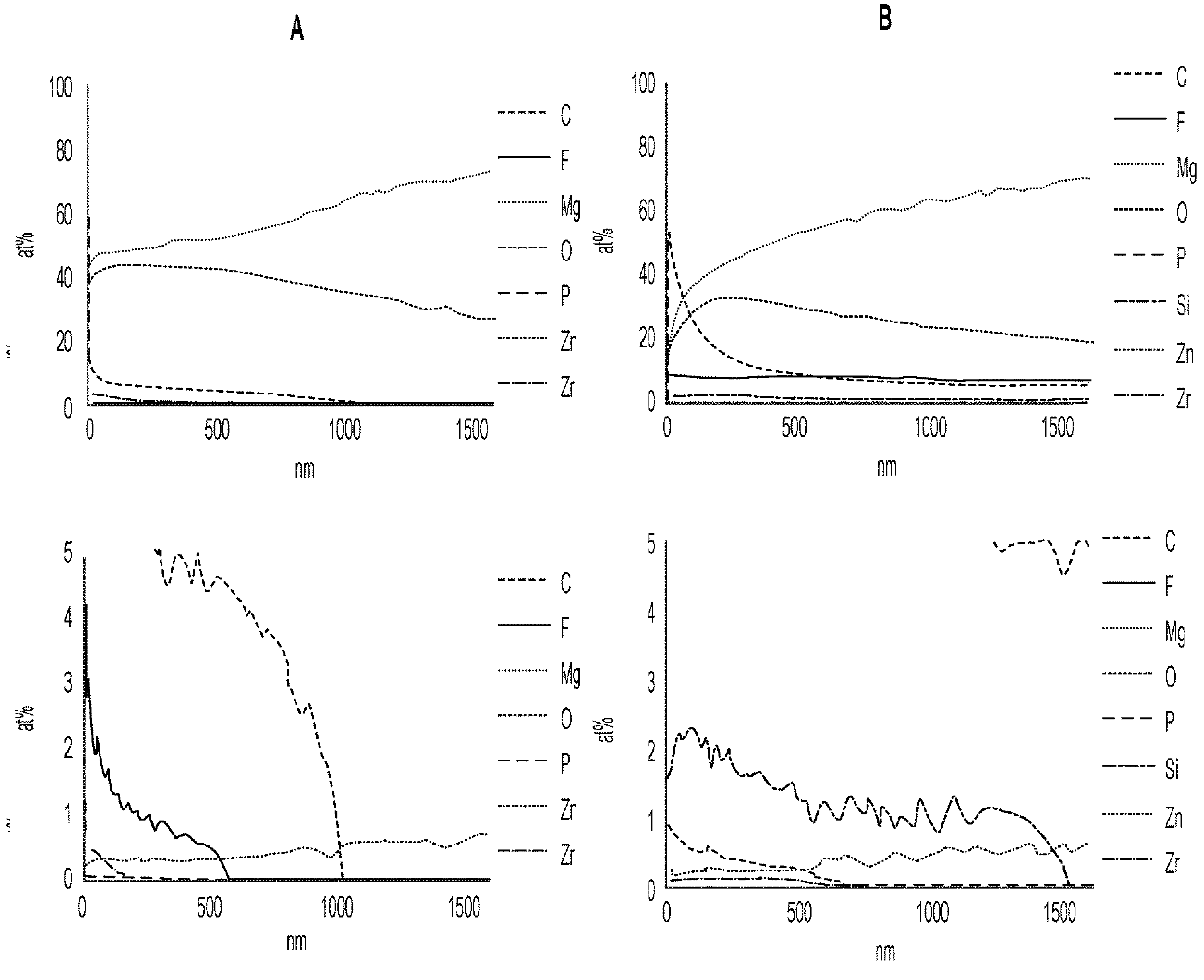
Publication Classification

(51) **Int. Cl.**
C23G 1/22 (2006.01)

(52) **U.S. Cl.**
CPC *C23G 1/22* (2013.01)

(57) **ABSTRACT**

Disclosed herein are systems and methods for treating a magnesium or a magnesium alloy substrate. The system includes a cleaning composition having a pH greater than 8.5 or a solvent, and a pretreatment composition comprising an organophosphate compound and/or an organophosphonate compound. The method includes contacting a substrate surface with the cleaning composition or the solvent, and contacting the surface with the pretreatment composition. Also disclosed are substrates treated with one of the systems or methods. Also disclosed are magnesium or magnesium alloy substrates wherein, between the air/substrate interface and 500 nm below the air/substrate interface (a) oxygen and magnesium are present in a combined amount of at least 70 atomic %; (b) carbon is present in an amount of no more than 30 atomic %; and/or (c) fluoride is present in an amount of no more than 8 atomic %, wherein atomic % is measured by XPS depth profiling.



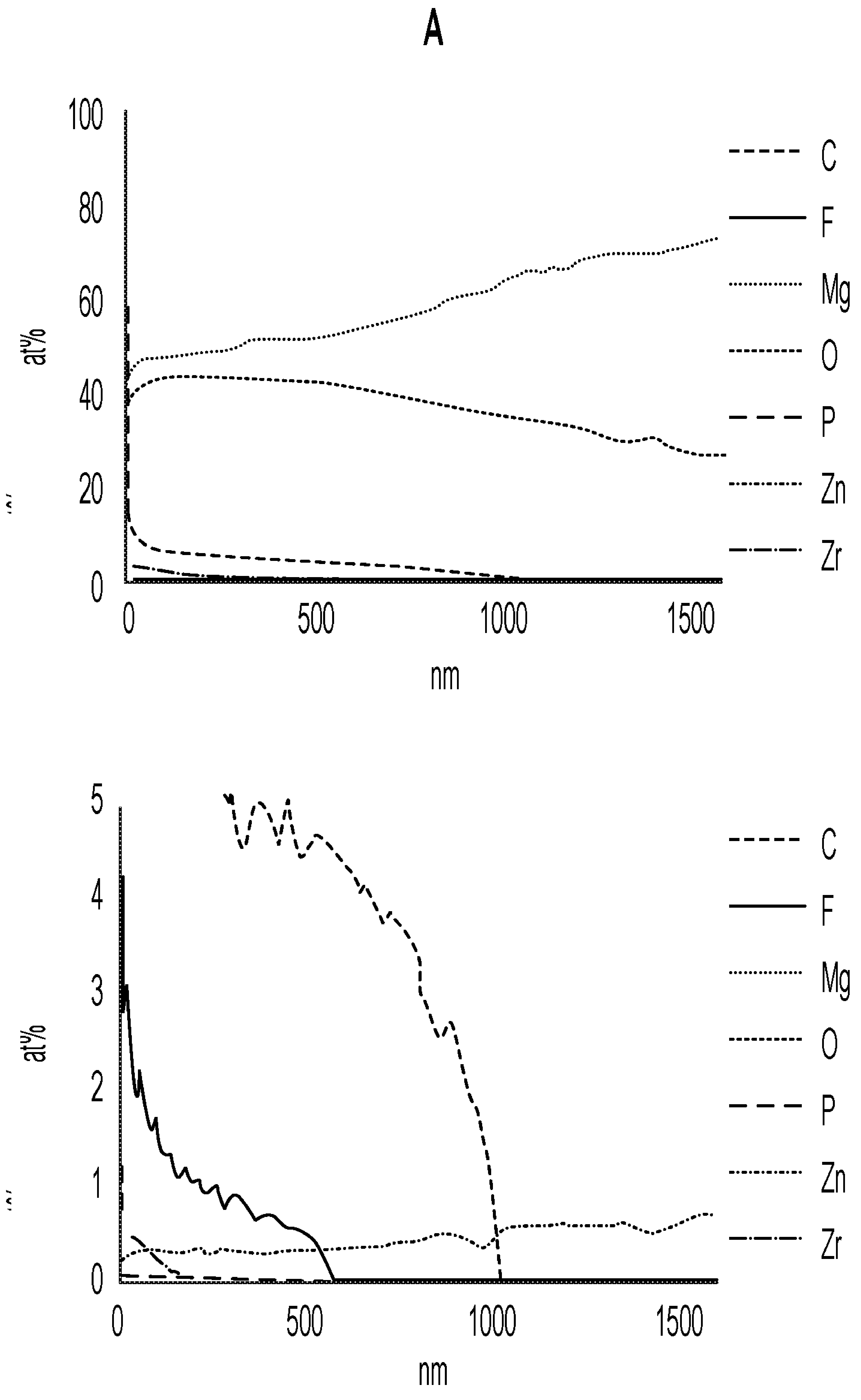

A
at%
100
80
60
40
20
0
0
500
1000
1500
nm
C
F
Mg
O
P
Zn
Zr
at%
5
4
3
2
1
0
0
500
1000
1500
nm
C
F
Mg
O
P
Zn
Zr

FIG. 1

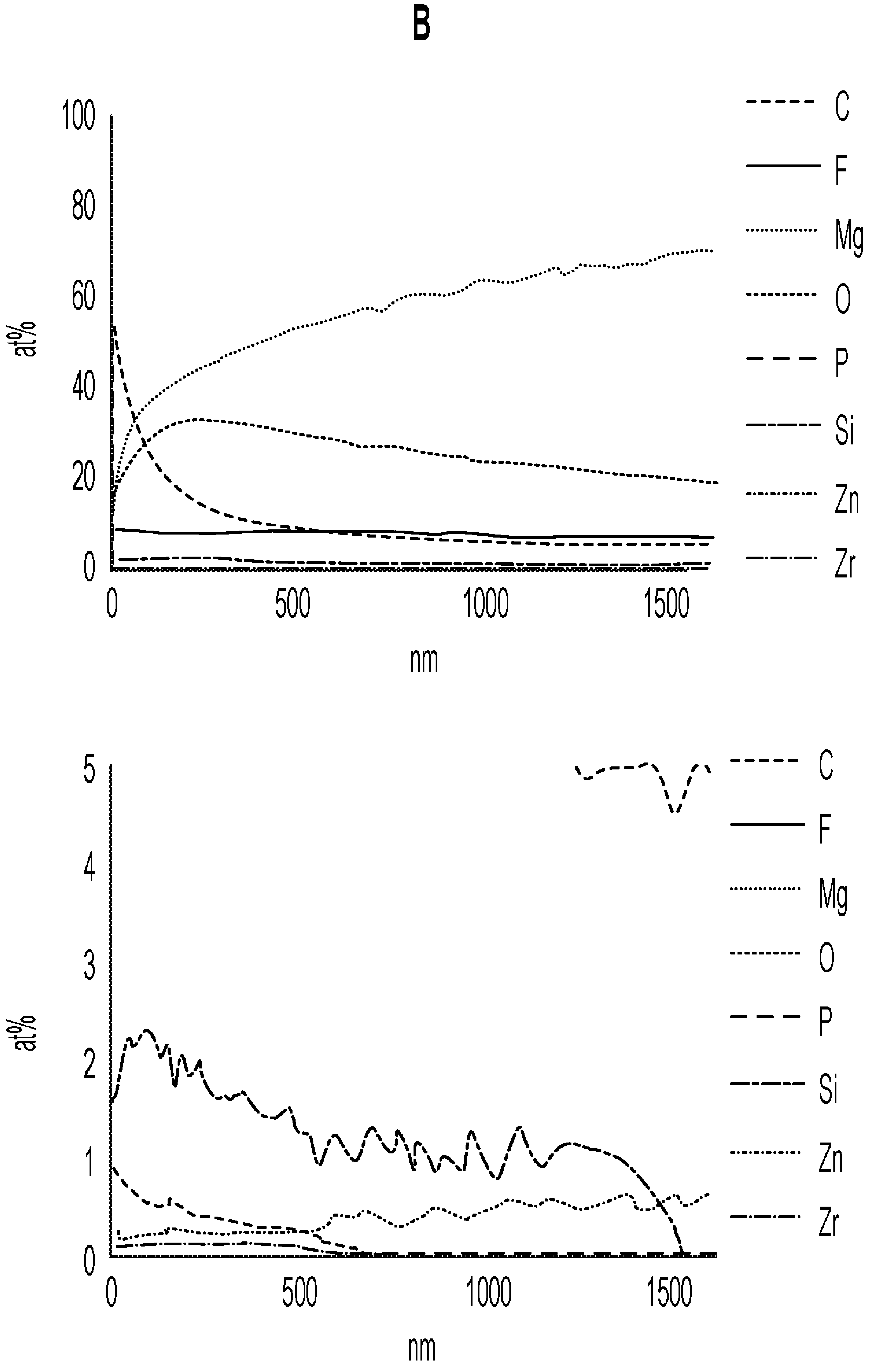

B
100
80
60
40
20
0
at%
0
500
1000
1500
nm
C
F
Mg
O
P
Si
Zn
Zr
5
4
3
2
1
0
at%
0
500
1000
1500
nm
C
F
Mg
O
P
Si
Zn
Zr

FIG. 1 (cont.)

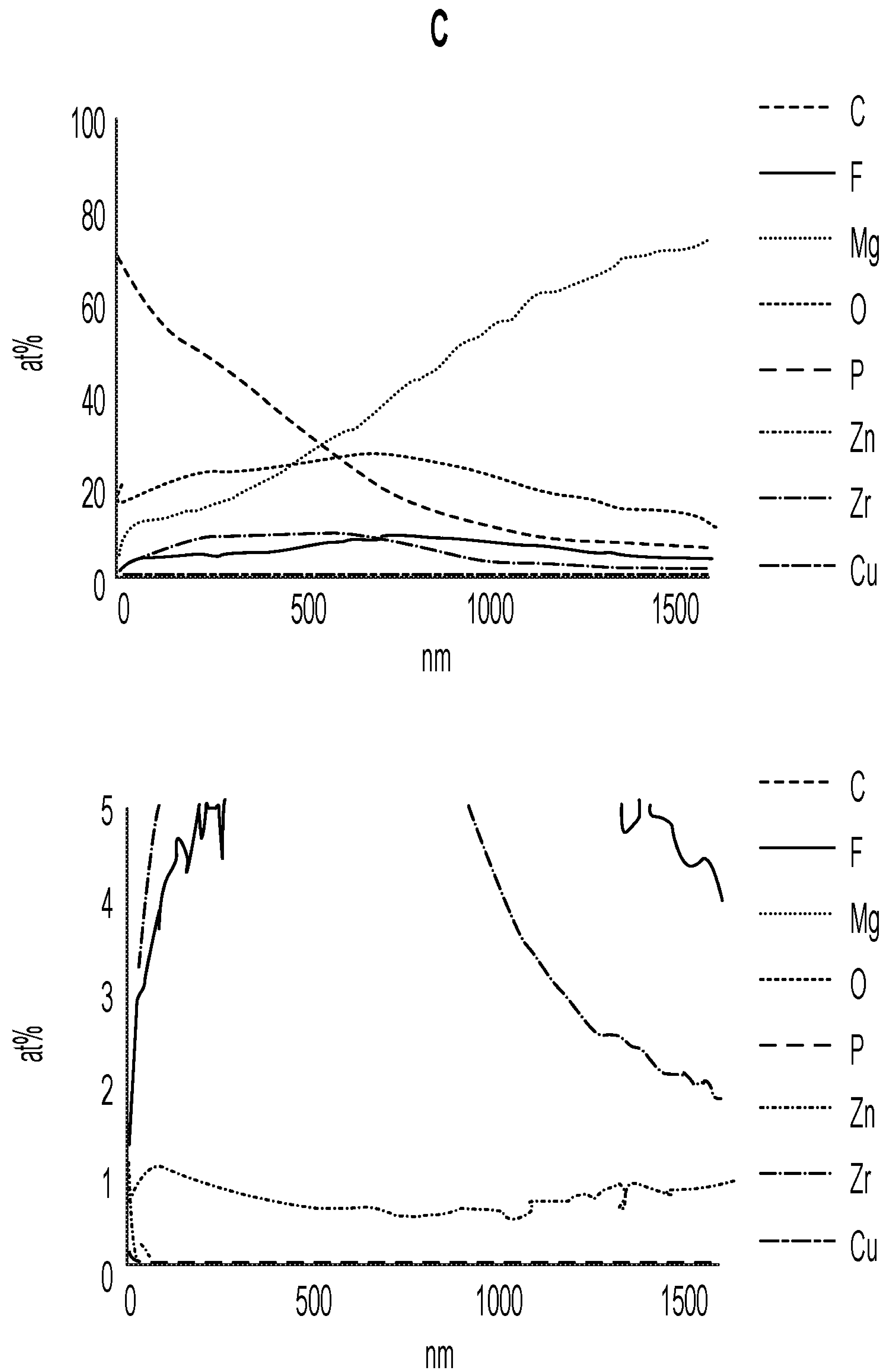

C
100
80
60
40
20
0
at%
0
500
1000
1500
nm
C
F
Mg
O
P
Zn
Zr
Cu
5
4
3
2
1
0
at%
0
500
1000
1500
nm
C
F
Mg
O
P
Zn
Zr
Cu

FIG. 1 (cont.)

SYSTEMS AND METHODS FOR TREATING A METAL SUBSTRATE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Application No. 62/913,482, filed on Oct. 10, 2019, and entitled "Systems and Methods for Treating a Substrate" and U.S. Provisional Application No. 62/913,500 filed on Oct. 10, 2019, and entitled "Systems and Methods for Treating a Substrate."

GOVERNMENT CONTRACT

[0002] This material is based upon work supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under Cooperative Agreement DE-EE007756 entitled U.S. Automotive Materials Partnership Low-Cost Mg Sheet Component Development and Demonstration Project.

FIELD OF THE INVENTION

[0003] The present invention relates to compositions, systems, and methods for treating a substrate.

BACKGROUND OF THE INVENTION

[0004] 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 OF THE INVENTION

[0005] Disclosed herein is a system for treating a substrate comprising: a cleaning composition having a pH greater than 8.5 or a solvent; and a pretreatment composition comprising an organophosphate compound, an organophosphonate compound, or combinations thereof, wherein the substrate comprises magnesium or a magnesium alloy.

[0006] Also disclosed herein is a method of treating a substrate comprising: contacting at least a portion of a surface of the substrate with a cleaning composition having a pH greater than 8.5 or a solvent; and contacting at least a portion of the surface with a pretreatment composition comprising an organophosphate compound, an organophosphonate compound, or combinations thereof, wherein the substrate comprises a magnesium or a magnesium alloy.

[0007] Also disclosed are substrates treated according to one of the systems and/or one of the methods of the present invention.

[0008] Also disclosed are substrates comprising a surface at least partially coated with a layer formed from one of the compositions disclosed herein.

[0009] Also disclosed are magnesium or magnesium alloy substrates, wherein (a) oxygen and magnesium are present between an air/substrate interface and 500 nm below the air/substrate interface in a combined amount of at least 70 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; (b) carbon is present between an air/substrate interface and 500 nm below the air/substrate interface in an amount of no more than 30 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; and/or (c) fluoride is present between an air substrate interface and 500 nm below the air/substrate interface in an amount of no more than 8 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer.

BRIEF DESCRIPTION OF THE FIGURES

[0010] FIG. **1** shows an XPS depth profile (A) of substrate treated according to Example 1, (B) of substrate treated with ST-2 according to comparative Example 2, and (C) of substrate treated with ST-6 according to Example 2.

DETAILED DESCRIPTION OF THE INVENTION

[0011] For purposes of the following detailed description, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers such as those expressing values, amounts, percentages, ranges, subranges and fractions may be read as if prefaced by the word "about," even if the term does not expressly appear. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Where a closed or open-ended numerical range is described herein, all numbers, values, amounts, percentages, subranges and fractions within or encompassed by the numerical range are to be considered as being specifically included in and belonging to the original disclosure of this application as if these numbers, values, amounts, percentages, subranges and fractions had been explicitly written out in their entirety.

[0012] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[0013] 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" Group IV metal and "a" solvent, a combination (i.e., a plurality) of these components can be used.

[0014] 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.

[0015] As used herein, "including," "containing" and like terms are understood in the context of this application to be synonymous with "comprising" and are therefore open-ended and do not exclude the presence of additional undescribed or unrecited elements, materials, ingredients or method steps. As used herein, "consisting of" is understood in the context of this application to exclude the presence of any unspecified element, ingredient or method step. As used herein, "consisting essentially of" is understood in the context of this application to include the specified elements, materials, ingredients or method steps "and those that do not materially affect the basic and novel characteristic(s)" of what is being described.

[0016] 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.

[0017] 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. As used herein, reference to a "first pretreatment composition," a "second pretreatment composition", and a "third pretreatment composition" is not intended to imply any specific order of treatment but rather is for ease of reference only.

[0018] As used herein, a "salt" refers to an ionic compound made up of metal cations and non-metallic anions and having an overall electrical charge of zero. Salts may be hydrated or anhydrous.

[0019] As used herein, "aqueous composition" refers to a solution or dispersion in a medium that comprises predominantly 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.

[0020] As used herein, the term "dispersion" refers to a two-phase transparent, translucent or opaque system in which metal phosphate particles are in the dispersed phase and an aqueous medium, which includes water, is in the continuous phase.

[0021] 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.

[0022] 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.

[0023] As used herein, the terms "Group IVB metal" and "Group IVB element" refer to an element that is in group IVB of the CAS version of the Periodic Table of the Elements as is shown, for example, in the Handbook of Chemistry and Physics, 63^{rd} edition (1983), corresponding to Group 4 in the actual IUPAC numbering.

[0024] As used herein, the term "Group IVB metal compound" refers to compounds that include at least one element that is in Group IVB of the CAS version of the Periodic Table of the Elements.

[0025] As used herein, a "coating composition" refers to a composition, e.g., a solution, 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.

[0026] 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 the coating composition is being applied to a substrate, e.g., at 10° C. to 40° C. and 5% to 80% relative humidity, while slightly thermal conditions are temperatures that are slightly above ambient temperature but are generally below the curing temperature for the coating composition (i.e. in other words, at temperatures and humidity conditions below which the reactive components will readily react and cure, e.g., >40° C. and less than 100° C. at 5% to 80% relative humidity).

[0027] 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 less than 2% by weight 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 less than 0.5% by weight 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 0% by weight of such material, or that such material is below the detection limit of common analytical techniques.

[0028] 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 carriers and solvents.

[0029] As used herein, the term "halogen" refers to any of the elements fluorine, chlorine, bromine, iodine, and astatine of the CAS version of the Periodic Table of the Elements, corresponding to Group VIIA of the periodic table.

[0030] As used herein, the term "halide" refers to compounds that include at least one halogen.

[0031] 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 carriers and solvents.

[0032] As mentioned above, the present invention is directed to a system for treating a metal substrate, the system comprising, or consisting essentially of, or consisting of: a cleaning composition having a pH greater than 8.5 or a solvent; and a pretreatment composition comprising, or consisting essentially of, or consisting of, an organophosphate compound, an organophosphonate compound, or combinations thereof, wherein in the substrate comprises magnesium or a magnesium alloy.

[0033] The present invention also is directed to a method of treating a metal substrate. 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 having a pH greater than 8.5 or a solvent; and then contacting at least a portion of the surface with a pretreatment composition comprising, or consisting essentially of, or consisting of, an organophosphate compound, an organophosphonate compound, or combinations thereof. 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. The metal substrate may comprise magnesium or a magnesium alloy. 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.

Substrates

[0034] Suitable substrates that may be used include magnesium and magnesium alloys of the AZXX (including Eform Plus), AMXX, EVXX, ZKXX, ZEXX, ZCXX, HKXX, HZXX, QEXX, QHXX, WEXX, ZEK100, or Elektron 21 series. Suitable substrates for use in the present invention include those that are often used in the assembly of vehicular 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, industrial structures and components such as appliances, including washers, dryers, refrigerators, stoves, dishwashers, and the like, personal electronics, agricultural equipment, lawn and garden equipment, air conditioning units, heat pump units, heat exchangers, 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, motorcycles, and/or trucks. The metal substrate also may be in the form of, for example, a sheet of metal or a fabricated part.

[0035] In examples, the substrate may be a multi-metal article. As used herein, the term "multi-metal article" refers to (1) an article that has at least one surface comprised of a first metal and at least one surface comprised of a second metal that is different from the first metal, (2) a first article that has at least one surface comprised of a first metal and a second article that has at least one surface comprised of a second metal that is different from the first metal, or (3) both (1) and (2).

[0036] 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.

Cleaners and Solvents

[0037] The system may comprise an alkaline cleaning composition for cleaning a substrate surface prior to treatment with a pretreatment composition (described below). In other examples, the substrate surface may be cleaned by solvent wiping the substrate surface prior to applying a pretreatment composition to the substrate. Nonlimiting examples of suitable solvents include ketones, such methyl ethyl ketone (MEK), methyl propyl ketone (MPK), acetone, methyl isobutyl ketone (MIBK), hexanes, heptanes, toluene, and the like.

[0038] At least a portion of the surface of the substrate may be cleaned by chemical means, such as cleaning/degreasing the surface with commercially available alkaline agents that are well known to those skilled in the art. Examples of alkaline cleaners suitable for use in the present invention include Chemkleen™ 166HP, 166M/C, 177, 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). Such cleaners are often preceded or followed by a water rinse, such as with tap water, distilled water, or combinations thereof.

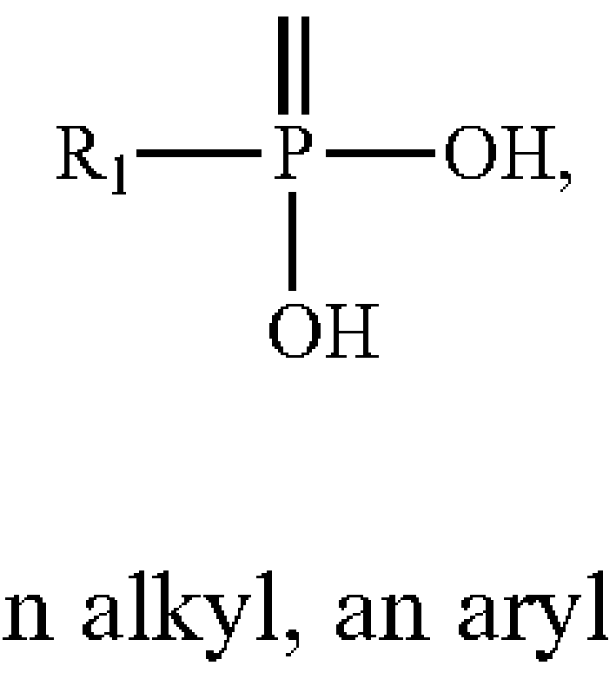
[0039] Following the cleaning step(s), the substrate optionally may be rinsed with tap water, deionized water, and/or an aqueous solution of rinsing agents in order to remove any residue. The wet substrate surface may be treated with a pretreatment composition (described below), or the substrate may 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.

[0040] The systems and methods disclosed herein may exclude any treatment compositions for treatment of the substrate surface between treatment with the alkaline cleaning composition and with the pretreatment composition, such as deoxidizers or acidic cleaner compositions.

Pretreatment Compositions

[0041] The pretreatment composition may comprise an organophosphate compound or an organophosphonate compound such as an organophosphoric acid or an organophosphonic acid. In examples, the organophosphate compound may be a phosphatized epoxy resin. In examples, the organophosphate or organophosphonate compound may be a phosphoric acid ester or a phosphonic acid ester of an epoxy compound.

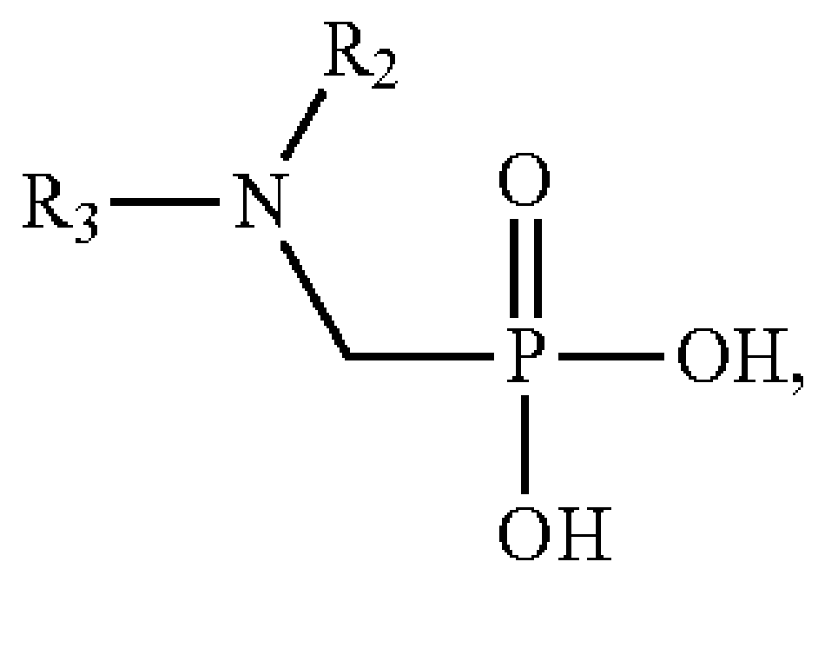
[0042] Suitable phosphoric acids include, but are not limited to, phosphoric acid ester of bisphenol A diglycidyl ether. Suitable phosphonic acids are those having at least one group of the structure:



$$R_1-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH,$$

where R_1 comprises an alkyl, an aryl, an alkoxide, an ester, and/or an ether. For example, R_1 may be CH_2 or O—CO—$(CH_2)_2$. Non-limiting examples include 1-hydroxyethyldiene-1,1-diphosphonic acid (HED), carboxyethyl phosphonic acid. Other examples of phosphonic acids include alkyl phosphonic acids where R_1 is an alkyl chain ranging from C_1

to C_6 such as methylphosphonic, ethylphosphonic acid, propylphosphonic acid, butylphosphonic acid, and/or hexylphosphonic acid. Phosphonic acids where R_1 is an aryl group such as phenylphosphonic acid may also be used. Examples of alpha-aminomethylene phosphonic acids which may be utilized in the reaction with an epoxy compound to prepare a compound of the invention include:



where R_2 comprises an alkyl, an aryl, an alkoxide, an ester, and/or an ether and R_3 comprises a hydrogen, an alkyl, an aryl, an alkoxide, an ester, an ether, and/or an epoxy. For example, R_2 may comprise $CH_2PO_3H_2$ and R_3 may comprise hydrogen or an alkyl group such as 2-hydroxyethyl, isopropyl, n-propyl, n-butyl, n-hexyl, n-octyl, isononyl, dodecyl, or benzyl. Other examples of alpha-aminomethylene phosphonic acids include examples where R_2 and R_3 are alkyl groups, such as P [(dimethylamino)methyl] phosphonic acid and P-[(diethylamino)methyl] phosphonic acid. Other examples of alpha-aminomethylene phosphonic acids with at least three phosphonic acid per molecule include: aminotris(methylenephosphonic acid) where R_2 and R; are $CH_2PO_3H_2$, ethylenediaminetetrakis(methylenephosphonic acid) i.e., $(H_2O_3PCH_2)_2N(CH_2)N(CH_2PO_3H_2)_2$, and diethylenetriaminepentakis(methylphosphonic acid), i.e., $[(H_2O_3PCH_2)_2N(CH_2)_2]_2NCH_2PO_3H_2$.

[0043] Alpha-aminomethylene phosphonic acids are generally known compounds and can be prepared utilizing generally known methods. Many alpha-aminomethylene phosphonic acids are available commercially, for example under the Dequest product line available from Italmatch Chemicals (Genoa, Italy). One such example is aminotris (methylenephosphonic acid) is available in an aqueous solution as Dequest 2000.

[0044] Suitable epoxy compounds include, but are not limited to, 1,2-epoxy compounds having an epoxy equivalence of at least 1, such as monoepoxides having a 1,2-epoxy equivalent of 1 or polyepoxides having a 1,2-epoxy equivalent of 2 or more. Examples of such epoxy compounds include, but are not limited to, polyglycidyl ethers of polyhydric phenols such as the polyglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane, i.e., bisphenol A, and 1,1-bis(4-hydroxyphenyl)isobutane, monoglycidyl ethers of a monohydric phenol or alcohol such as phenyl glycidyl ether and butyl glycidyl ether, or combinations thereof.

[0045] Suitable examples of organophosphonic or organophosphoric resins include, but are not limited to, benzylaminobis(methylenephosphonic) acid ester of bisphenol A diglycidyl ether carboxyethyl phosphonic acid ester of bisphenol A diglycidyl ether and of phenylglycidyl ether and of butyl glycidyl ether; carboxyethyl phosphonic acid mixed ester of bisphenol A diglycidyl ether and butylglycidyl ether; triethoxyl silyl propylaminobis(methylenephosphonic) acid ester of bisphenol A diglycidyl ether and cocoaminobis (methylenephosphonic) acid ester of bisphenol A diglycidyl ether.

[0046] The organophosphate or organophosphonate compound may be present in the pretreatment composition in an amount of 1 percent by weight based on total weight of the pretreatment composition, such as 5 percent by weight, and may be present in an amount of no more than 20 percent by weight based on total weight of the pretreatment composition, such as no more than 15 percent by weight. The organophosphate or organophosphonate compound may be present in the pretreatment composition in an amount of 1 percent by weight to 20 percent by weight based on total weight of the pretreatment composition, such as 5 percent by weight to 15 percent by weight.

[0047] The pretreatment composition may have a solids content of 1.25 percent based on total weight of the pretreatment composition, such as 2.5 percent, such as 5 percent, and may have a solids content of no more than 25 percent based on total weight of the pretreatment composition, such as no more than 15 percent, such as no more than 10 percent. The pretreatment composition may have a solids content of 1.25 percent to 25 percent based on total weight of the pretreatment composition, such as 2.5 percent to 15 percent, such as 5 percent to 10 percent.

[0048] The organophosphate or organophosphonate compound may be soluble in an aqueous medium (described below) to the extent of at least 0.03 grams per 100 grams of water at 25° C.

[0049] The pretreatment composition optionally may further comprise at least one Group IVB metal.

[0050] The Group IVB metal cation may comprise zirconium, titanium, hafnium, or combinations thereof. Suitable compounds of zirconium include, but are not limited to, hexafluorozirconic acid, alkali metal and ammonium salts thereof, ammonium zirconium carbonate, zirconyl nitrate, zirconyl sulfate, zirconium carboxylates and zirconium hydroxy carboxylates, such as zirconium acetate, zirconium oxalate, ammonium zirconium glycolate, ammonium zirconium lactate, ammonium zirconium citrate, zirconium basic carbonate, zirconium tetraalkaloids, and mixtures thereof. Suitable compounds of titanium include, but are not limited to, fluorotitanic acid and its salts. A suitable compound of hafnium includes, but is not limited to, hafnium nitrate.

[0051] According to the present invention, the Group IVB metal may be present in the pretreatment composition in a total amount of at least 1 ppm metal based on total weight of the pretreatment composition, such as at least 10 ppm metal, such as at least 20 ppm metal. According to the present invention, the Group IVB metal may be present in the pretreatment composition in a total amount of no more than 800 ppm metal based on total weight of the pretreatment composition, such as no more than 450 ppm metal, such as no more than 200 ppm metal. According to the present invention, the Group IVB metal may be present in the pretreatment composition in a total amount of 1 ppm to 800 ppm metal based on total weight of the pretreatment composition, such as 10 ppm to 450 ppm, such as 20 ppm to 200 ppm. As used herein, the term "total amount," when used with respect to the amount of Group IVB metal in the pretreatment composition, means the sum of all Group IVB metals present in the pretreatment composition. Alternatively, the pretreatment composition may be substantially free, or essentially free, or completely free, of Group IVB metals.

[0052] In other examples, the pretreatment composition and/or the system may be substantially free, or, in some cases, essentially free, or in some cases, completely free of any Group IVB metals.

[0053] The pretreatment composition optionally may further comprise a halide ion, such as, for example, fluoride or chloride. Suitable sources of free fluoride (defined herein below) or chloride ions include hydrofluoric acid, hydrochloric acid, fluorosilicic acid, sodium hydrogen fluoride, potassium hydrogen fluoride, ammonium salts of halides, and/or acids or salts of tetrafluoroborate. Complex fluoride containing compounds such as fluorotitanic acid, fluorozirconic acid, potassium hexafluorotitanate and potassium hexafluorozirconate can also be used. The acidic fluoride or chloride compounds may be present in the pretreatment composition in amounts of at least 300 ppm based on total weight of the pretreatment, such as at least 400 ppm, such as at least 500 ppm, such as at least 800 ppm, and may be present in an amount of no more than 3500 ppm based on total weight of the pretreatment composition, such as no more than 2000 ppm, such as no more than 1500 ppm, such as no more than 1200 ppm. The acidic fluoride or chloride compounds may be present in the pretreatment composition in amounts of 300 ppm to 3500 ppm based on total weight of the pretreatment composition, such as 400 ppm to 2000 ppm, such as 500 ppm to 1500 ppm, such as 800 ppm to 1200 ppm.

[0054] That is, the pretreatment composition may comprise free fluoride. As used herein the amount of fluoride disclosed or reported in the first pretreatment composition is referred to as "free fluoride," that is, fluoride present in the first pretreatment composition that is not bound to metal ions or hydrogen ions, as measured in parts per million of fluoride. Free fluoride is defined herein as being able to 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, 247-250, 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 can be read directly.

[0055] The free fluoride of the pretreatment composition may be present in an amount of at least 1 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 200 ppm. According to the present invention, the free fluoride of the pretreatment composition may be present in an amount of no more than 2,500 ppm based on a total weight of the pretreatment composition, such as no more than 1,000 ppm, such as no more than 600 ppm. According to the present invention, the free fluoride of the pretreatment composition may be present in an amount of 1 ppm to 2,500 ppm based on a total weight of the pretreatment composition, such as 50 ppm to 1,000 ppm, such as 200 ppm to 600 ppm.

[0056] In other examples, the pretreatment composition and/or the system may exclude fluoride or fluoride sources. As used herein, "fluoride sources" include monofluorides, bifluorides, fluoride complexes, and mixtures thereof known to generate fluoride ions. When a composition and/or a layer or coating comprising the same or a system is substantially free, essentially free, or completely free of fluoride, this means that fluoride ions or fluoride sources in any form are excluded from the composition or system, except that unintentional fluoride that may be present in a composition or bath containing the composition as a result of, for example, carry-over from prior treatment baths in the processing line, municipal water sources (e.g.: fluoride added to water supplies to prevent tooth decay), fluoride from a pretreated substrate, or the like. That is, a bath that is substantially free, essentially free, or completely free of fluoride, may have unintentional fluoride that may be derived from these external sources, even though the composition or compositions making up the system and used to make the bath prior to use on the processing line was substantially free, essentially free, or completely free of fluoride.

[0057] For example, the pretreatment composition and/or the compositions making up the system may be substantially free of any fluoride-sources, such as ammonium and alkali metal fluorides, acid fluorides, fluoroboric, fluorosilicic, fluorotitanic, and fluorozirconic acids and their ammonium and alkali metal salts, and other inorganic fluorides, nonexclusive examples of which are: zinc fluoride, zinc aluminum fluoride, titanium fluoride, zirconium fluoride, nickel fluoride, ammonium fluoride, sodium fluoride, potassium fluoride, and hydrofluoric acid, as well as other similar materials known to those skilled in the art.

[0058] The pretreatment composition may further comprise a foam depressor, including by way of non-limiting example Foam Depressor 304 CK (commercially available from PPG Industries, Inc.). Those skilled in the art of pretreatment technologies understand that foam in a pretreatment bath may have a negative impact on substrate wetting and the appearance or quality of a film formed by a pretreatment composition. Accordingly, foam depressors may be added to a cleaning and pretreatment compositions to prevent the formation of foam or to break foam already present, particularly in spray applications. Defoaming surfactants may optionally be present at levels up to 1 weight percent, such as up to 0.1 percent by weight, and wetting agents are typically present at levels up to 2 percent, such as up to 0.5 percent by weight, based on the total weight of the pretreatment composition.

[0059] The pretreatment composition may optionally be substantially free, essentially free, or completely free of copper.

[0060] The pretreatment composition may have a pH of less than 6, such as 2 to 6, such as 2.5 to 5.5, and may be adjusted using, for example, any acid and/or 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 pretreatment 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 triethylamine, methylethyl amine, or mixtures thereof.

[0061] The pretreatment composition may be an aqueous composition. 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 invention, the solution or dispersion, may be in contact with at least a portion of a surface of the substrate for at least 5 seconds, such as at least 45 seconds, such at least 60 seconds, such as at least 120 seconds, such as at least 180 seconds, such as for 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. to 49° C.

[0062] The pretreatment composition may optionally contain other materials in addition to those described above, such as nonionic surfactants and auxiliaries conventionally used in the art of pretreatment. In an aqueous medium, water dispersible organic solvents, for example, alcohols with up to about 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; a base such as an amine which can partially or completely neutralize the organophosphate or organophosphonate compound to enhance the solubility of the organophosphate or organophosphonate compounds, such as diisopropanolamine, triethylamine, dimethylethanolamine, and 2-amino-2-methylpropanol; 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.

[0063] 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, perchlorinate ions, chlorate ions, chlorite ions as well as ascorbic acid, citric acid, tartaric acid, malonic acid, succinic acid and salts thereof.

[0064] The pretreatment composition and/or the system may exclude chromium or chromium-containing compounds. As used herein, the term "chromium-containing compound" refers to materials that include 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, and strontium dichromate. When a composition and/or a coating or a layer formed from the same, or a system, is substantially free, essentially free, or completely free of chromium, this includes chromium in any form, such as, but not limited to, the hexavalent chromium-containing compounds listed above.

[0065] Thus, optionally, the pretreatment composition and/or coatings or layers deposited from the same, and/or the system, 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 listed in the preceding paragraph. A composition and/or coating or layer formed from the same and/or a system that is substantially free of chromium or derivatives thereof means 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 composition or the system; in the case of chromium, this may further include that the element or compounds thereof are not present in the composition and/or coatings or layers formed from the same and/or system in such a level that it causes a burden on the environment. The term "substantially free," when used herein with respect to a pretreatment composition, means that the composition and/or coatings or layers formed from the same contain 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 coating or layer, respectively, if any at all. The term "essentially free," when used herein with respect to a pretreatment composition, means that the composition and/or coatings or layers formed from the same contain 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 herein with respect to a pretreatment composition, means that the composition and/or coatings or layers formed from the same contain less than 1 ppb of any or all of the elements or compounds listed in the preceding paragraph, if any at all. The term "substantially free," when used herein with respect to the system, means that each composition comprising the system and/or coatings or layers formed from each such composition contain 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 coating or layer, respectively, if any at all. The term "essentially free," when used herein with respect to the system, means that each composition comprising the system and/or coatings or layers formed from each such composition contain 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 herein with respect to the system, means that each composition comprising the system and/or coatings or layers formed from each such composition contain less than 1 ppb of any or all of the elements or compounds listed in the preceding paragraph, if any at all.

[0066] Following the contacting with a pretreatment composition disclosed herein, the substrate optionally may be air dried at room temperature or may be dried with hot air, for example, by using an air knife, by flashing off the water by brief exposure of the substrate to a high temperature, such as by drying the substrate in an oven at 15° C. to 200° 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. Following the contacting with a pretreatment composition disclosed herein, 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 and then optionally may be dried, for example air dried or dried with hot air as described in the preceding sentence, "such as by drying the substrate in an oven at 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. Following the contacting with a pretreatment composition disclosed herein, and any optional rinsing stages, a coating composition comprising a film-forming resin may be deposited onto at least a portion of the surface of the wet substrate by any suitable technique, including, for example, brushing, dipping, flow coating, spraying and the like.

Film-Forming Resins

[0067] Optionally, the system of the present invention may further comprise 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.

[0068] 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 crosslinking reaction of the composition constituents often induced, for example, by heat or radiation. Curing or crosslinking reactions also may be carried out under ambient conditions. Once cured or crosslinked, a thermosetting resin will not melt upon the application of heat and is insoluble in solvents. As used herein, the term "thermoplastic" refers to resins that comprise polymeric components that are not joined by covalent bonds and thereby can undergo liquid flow upon heating and are soluble in solvents.

[0069] As previously indicated, 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.

[0070] 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 U.S. Patent Application Publication No. 2009-0045071 at [0004]-[0015] and U.S. patent application Ser. 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 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.

[0071] 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.

[0072] The electrodepositable coating composition may further comprise other optional ingredients, such as a pigment composition and, if desired, various additives such as fillers, plasticizers, anti-oxidants, biocides, UV light absorbers and stabilizers, hindered amine light stabilizers, defoamers, fungicides, dispersing aids, flow control agents, surfactants, wetting agents, or combinations thereof.

[0073] 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.

[0074] 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 electrodepositable 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.

[0075] Once the cationic or anionic electrodepositable 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.). For anionic electrodeposition, the coated substrate may be heated to a temperature ranging from 200° F. to 450° F. (93° 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 to 40 minutes. The thickness of the resultant cured electrodeposited coating may range from 10 to 50 microns.

[0076] 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 invention include the polyester-based ENVIROCRON line of powder coating compositions (commercially available from PPG Industries, Inc.) or epoxy-polyester hybrid powder coating compositions. Alternative examples of powder coating compositions that may be used 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 U.S. Pat. No. 7,470,752, assigned to PPG Industries, Inc. and incorporated herein by reference); curable powder coating compositions generally comprising (a) at least one tertiary aminourea compound, at least one tertiary aminourethane compound, or mixtures thereof, and (b) at least one film-forming epoxy-containing resin and/or at least one siloxane-containing resin (such as those described in U.S. Pat. No. 7,432,333, 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 U.S. Pat. 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 15 minutes to 25 minutes. The thickness of the resultant film is from 50 microns to 125 microns.

[0077] 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.

[0078] 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 of 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® line of solvent-based coating compositions, the AQUACRON® line of water-based coating compositions, and the RAYCRON® 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 isocyanurate, a (poly) urea, a (poly)epoxy, an anhydride, an acrylic, a (poly)ether, a (poly)sulfide, a (poly)amine, a (poly)amide, (poly)vinyl chloride, (poly)olefin, (poly)vinylidene fluoride, (poly)siloxane, or combinations thereof.

[0079] 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 examples, chromate-based primers and/or advanced performance topcoats. 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). Alternately, the primer coat can be a chromate-free primer coat, such as the coating compositions described in U.S. patent application Ser. No. 10/758,973, titled "CORROSION RESISTANT COATINGS CONTAINING CARBON", and U.S. patent application Ser. Nos. 10/758,972, and 10/758,972, both titled "CORROSION RESISTANT COATINGS", all of which are incorporated herein by reference, and 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 invention.

[0080] As mentioned above, the substrate of the present invention also may 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 (Deft 03W127A and Deft 03GY292). The topcoat may be an advanced performance topcoat, such as those available from PPG (Defthane® ELT™ 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.

[0081] 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 a "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 that conform to TT-P-2756A. Examples of self-priming topcoats include those available from PPG (03W169 and 03GY369), and examples of enhanced self-priming topcoats include Defthane® ELT™/ESPT and product code number 97GY121, available from PPG. 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.

[0082] 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.

[0083] 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.

[0084] In addition, a colorant and, if desired, various additives such as surfactants, wetting agents or catalyst can be included in the coating composition (electrodepositable, powder, or liquid). As used herein, the term "colorant" means any substance that imparts color and/or other opacity and/or other visual effect to the composition. 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 from 1 to 65 weight percent, such as from 3 to 40 weight percent or 5 to 35 weight percent, with weight percent based on the total weight of the composition.

Methods

[0085] Also disclosed herein is a method of treating a substrate, comprising, or consisting essentially of, or contacting at least a portion of a surface of the substrate with an alkaline cleaning composition having a pH of at least 8.5 or a solvent; and contacting at least a portion of the contacted surface with a pretreatment composition comprising, or consisting essentially of, or consisting of, an organophosphate compound and/or an organophosphonate compound. Optionally, the method may exclude contacting the substrate surface with any treatment compositions (excluding water rinses) between the alkaline cleaning composition and the pretreatment composition, such as deoxidizers, acidic cleaner compositions, or other treatment compositions.

[0086] The contacting with the pretreatment composition may be for at least 5 seconds, such as at least 45 seconds, such at least 60 seconds, such as at least 120 seconds, such as at least 180 seconds, such as for 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. to 49° C.

Treated Substrates

[0087] XPS depth profiling data are reported in FIG. **1**. The XPS depth profile of the substrates were generated using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons (<5 eV) and argon ions. The binding energy axis was calibrated using sputter cleaned Cu foil (Cu 2p3/2=932.62 eV, Cu 2p3/2=75.1 eV) and Au foils (Au 4f7/2=83.96 eV). Peaks were charge referenced to CHx band in the carbon is spectra at 284.8 eV. Measurements were made at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3-6 nm (95% of the signal originated from this depth or shallower). Quantification was done using instrumental relative sensitivity factors (RSFs) that account for the x-ray cross section and inelastic mean free path of the electrons. Ion sputtering was done using 2 kV Ar+ rastered over a 2 mm×2 mm area. The sputtering rate in the Al_2O_3 layer was 9.5 nm/min.

[0088] Also disclosed herein is a substrate treated by one of the systems and/or methods of the present invention. The treated substrate surprisingly may comprise oxygen and magnesium between an air/substrate interface and 500 nm below the air/substrate interface in a combined amount of at least 70 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer, such as 70 atomic % to 85 atomic %.

[0089] The treated substrate also may comprise carbon between an air/substrate interface and 500 nm below the air/substrate interface in an amount of no more than 30 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer, such as 15 atomic % to 30 atomic %.

[0090] The treated substrate also may comprise fluoride is present between an air substrate interface and 500 nm below the air/substrate interface in an amount of no more than 8 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer, such as 3 atomic % to 8 atomic %.

[0091] These were unexpected results achieved by treatment of the substrate with a system or a method disclosed herein.

[0092] The substrate having the film formed on the substrate by contacting the surface with a surface treatment composition comprising an alkaline cleaning composition or a solvent and a pretreatment composition disclosed herein improves corrosion performance (i.e., scribe creep) on the substrate surface compared to a substrate treated with an alkaline cleaning composition, a chemical deoxidation composition, and a pretreatment composition. That is, elimination of the treatment of the substrate surface with a chemical deoxidizing composition significantly improved corrosion performance.

[0093] Also disclosed is a magnesium substrate, wherein (a) oxygen and magnesium are present between an air/substrate interface and 500 nm below the air/substrate interface in a combined amount of at least 70 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; (b) carbon is present between an air/substrate interface and 500 nm below the air/substrate interface in an amount of no more than 30 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; and/or (c) fluoride is present between an air substrate interface and 500 nm below the air/substrate interface in an amount of no more than 8 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer.

[0094] Whereas specific aspects of the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular arrangements disclosed are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the full breadth of the claims and aspects appended and any and all equivalents thereof.

[0095] In view of the foregoing description the present invention thus relates in particular, without being limited thereto, to the following Aspects 1-30:

ASPECTS

[0096] Aspect 1. A system for treating a substrate comprising:

- **[0097]** a cleaning composition having a pH greater than 8.5 or a solvent; and
- **[0098]** a pretreatment composition comprising an organophosphate compound, an organophosphonate compound, or combinations thereof, wherein in the substrate comprises magnesium or a magnesium alloy.

[0099] Aspect 2. The system of Aspect 1, wherein the cleaning composition has a pH of at least 10.

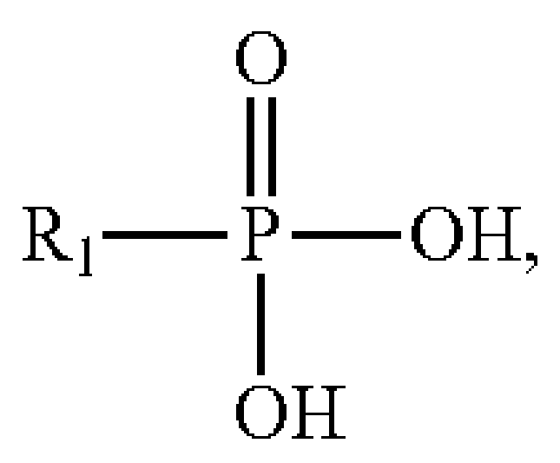
[0100] Aspect 3. The system of Aspect 1 or Aspect 2, wherein the pretreatment composition has a solids content of 1.25% to 25% by weight based on total weight of the pretreatment composition.

[0101] Aspect 4. The system of any of the preceding Aspects, wherein the pretreatment composition has a pH of 2 to 6.

[0102] Aspect 5. The system of any of the preceding Aspects, wherein the organophosphate compound comprises a phosphatized epoxy.

[0103] Aspect 6. The system of Aspect 5, wherein the phosphatized epoxy comprises a phosphoric acid ester and/or a phosphonic acid ester of an epoxy compound.

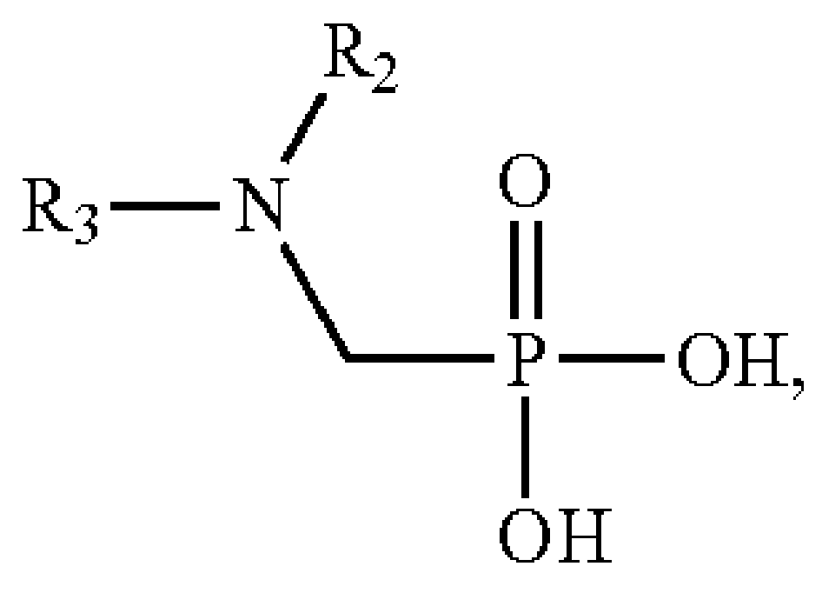
[0104] Aspect 7. The system of any of the preceding Aspects, wherein the organophosphonate compound comprises a phosphoric acid or a phosphonic acid comprising at least one group of the structure



$$R_1-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH,$$

wherein R_1 comprises an alkyl, an aryl, an alkoxide, an ester, and/or an ether.

[0105] Aspect 8. The system of any of Aspects 1 to 6, wherein the organophosphonate compound comprises a phosphoric acid or a phosphonic acid comprising the structure



wherein R_2 comprises an alkyl, an aryl, an alkoxide, an ester, and/or an ether and R_3 comprises a hydrogen, an alkyl, an aryl, an alkoxide, an ester, an ether, and/or an epoxy.

[0106] Aspect 9. The system of any of the preceding Aspects, wherein the organophosphate compound and/or the organophosphonate compound are present in an amount of 1 percent by weight to 20 percent by weight based on total weight of the pretreatment composition.

[0107] Aspect 10. The system of any of the preceding Aspects, wherein the pretreatment composition further comprises a Group IVB metal.

[0108] Aspect 11. The system of Aspect 10, wherein the Group IVB metal is present in an amount of 1 ppm to 800 ppm based on total weight of the pretreatment composition.

[0109] Aspect 12. The system of any of the preceding Aspects, wherein the pretreatment composition further comprises free fluoride.

[0110] Aspect 13. The system of Aspect 12, wherein the free fluoride is present in an amount of 1 ppm to 2,500 ppm based on total weight of the pretreatment composition.

[0111] Aspect 14. The system of any of the preceding Aspects, wherein the pretreatment composition further comprises a halide and/or a reaction accelerator.

[0112] Aspect 15. The system of any of the preceding Aspects, wherein the pretreatment composition is substantially free, essentially free, or completely free of copper and/or chromium.

[0113] Aspect 16. The system of any of Aspects 1 to 11, 14, or 15, wherein the pretreatment composition is substantially free, essentially free, or completely free of fluoride.

[0114] Aspect 17. The system of any of Aspects 1 to 9 or 12 to 16, wherein the pretreatment composition is substantially free of a Group IVB metal.

[0115] Aspect 18. The system of any of the preceding Aspects, further comprising a film-forming composition.

[0116] Aspect 19. The system of Aspect 18, wherein the film-forming composition comprises an anionic electrodepositable coating composition, a cationic electrodepositable coating composition, a powder coating composition, a liquid coating composition, a primer composition, and/or a topcoat composition.

[0117] Aspect 20. A method of treating a substrate comprising: contacting at least a portion of a surface of the substrate with the cleaner or the solvent of the system of any of the preceding Aspects; and contacting at least a portion of the surface with the pretreatment composition of any of the preceding Aspects.

[0118] Aspect 21. The method of Aspect 20, wherein the substrate is optionally rinsed with water between contacting the substrate surface with the cleaning composition or the solvent and contacting the substrate surface with the pretreatment composition; optionally without contacting the substrate surface with a surface treatment composition prior to contacting with the pretreatment composition; wherein the metal substrate comprises magnesium or a magnesium alloy.

[0119] Aspect 22. The method of Aspect 20 or Aspect 21, wherein the contacting with the pretreatment composition is for 5 sec to 5 min and/or wherein the pretreatment composition is a temperature of 21° C. to 49° C.

[0120] Aspect 23. The method of any of Aspects 20 to 22, further comprising contacting at least a portion of the substrate surface with the film-forming composition following the contacting with the pretreatment composition.

[0121] Aspect 24. A magnesium substrate, wherein (a) oxygen and magnesium are present between an air/substrate interface and 500 nm below the air/substrate interface in a combined amount of at least 70 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; (b) carbon is present between an air/substrate interface and 500 nm below the air/substrate interface in an amount of no more than 30 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; and/or (c) fluoride is present between an air substrate interface and 500 nm below the air/substrate interface in an amount of no more than 8 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer.

[0122] Aspect 25. A treated substrate, wherein at least a portion of the substrate is treated with the system of any of Aspects 1 to 19 or according to the method of any of Aspects 20 to 24, wherein the substrate comprises magnesium or a magnesium alloy.

[0123] Aspect 26. The treated substrate of Aspect 25, wherein (a) oxygen and magnesium are present between an air/substrate interface and 500 nm below the air/substrate interface in a combined amount of at least 70 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; (b) carbon is present between an air/substrate interface and 500 nm below the air/substrate interface in an amount of no more than 30 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; and/or (c) fluoride is present between an air substrate interface and 500 nm below the air/substrate interface in an amount of no more than 8 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer.

[0124] Aspect 27. The substrate of any of Aspects 24 to 26, wherein the substrate comprises a vehicle, a part, an article, a heat exchanger, an appliance, a personal electronic device, a multi-metal article, or combinations thereof.

[0125] Aspect 28. The substrate of Aspect 27, wherein the vehicle comprises an automobile or an aircraft.

[0126] Aspect 29. The substrate of any of Aspects 24 to 28, wherein the substrate comprises a three-dimensional component formed by an additive manufacturing process.

[0127] Aspect 30. The substrate of Aspect 29, wherein the additive manufacturing process comprises selective laser melting, e-beam melting, directed energy deposition, metal extrusion, and/or binder jetting.

[0128] Illustrating the invention are the following examples, which, however, are not to be considered as limiting the invention to their details. Unless otherwise indicated, all parts and percentages in the following examples, as well as throughout the specification, are by weight

EXAMPLES

Preparation of Cleaners, Pretreatment Compositions, and Electrocoats Used in Examples 1 and 2

[0129] Preparation of Cleaner Composition 1 (ST-1): A rectangular stainless-steel tank with a total volume of 37 gallons, equipped with Vee-jet nozzles, was filled with 10 gallons of deionized water. To this was added 475 mL of Chemkleen 2010LP (a phosphate-free alkaline cleaner commercially available from PPG Industries, Inc.) and 47.5 mL of Chemkleen 181ALP (a phosphate-free blended surfactant additive commercially available from PPG Industries, Inc.). The 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 composition. The pH of ST-1 was 12.30. The bath was used to spray clean and degrease panels for 120 seconds at 10-15 psi.

[0130] Preparation of Cleaner Composition 2 (ST-2): A bath containing Chemkleen Surface Prep 1 was prepared in a 2-gallon bucket according to manufacturer's instructions with Chemkleen Surface Prep 1 concentrate (80 g) (1%) (an alkaline cleaner commercially available from PPG Industries, Inc.) and Chemkleen 185A (80 g) (1%) (a phosphate-free blended surfactant package commercially available from PPG Industries, Inc.) in DI water. pH was measured as described above with respect to ST-1. ST-2 had a pH of 12.37. The bath was used to immersion clean and degrease panels for 120 seconds.

[0131] Preparation of Cleaner Composition 3 (ST-3): A bath containing Chemkleen 490MX was prepared in a 2-gallon bucket according to manufacturer's instructions with Chemkleen 490MX powder (1%) (an alkaline cleaner commercially available from PPG Industries, Inc.) in DI water. pH was measured as described above with respect to ST-1. ST-3 had a pH of 11.58. The bath was used to immersion clean and degrease panels for 120 seconds.

[0132] Preparation of Surface Treatment 4 (ST-4): A bath containing ChemDeox 395 was prepared in a 3-gallon bucket according to manufacturer's instructions with ChemDeox 395A (10.05 g/L) (an acidic deoxidizer activation package commercially available from PPG Industries, Inc.) and ChemDeox 395B (22.75 g/L) (an alkaline deoxidizer activation package commercially available from PPG Industries, Inc.) in DI water.

[0133] Preparation of Surface Treatment 5 (ST-5): A bath containing ChemDeox 395A was prepared according to manufacturer's instructions (an acidic deoxidizer activation package commercially available from PPG Industries, Inc.) and the pH was adjusted to a range of 2.4 to 2.5 with 89.62 g of Chemfil Buffer (an alkaline buffering solution, commercially available from PPG Industries, Inc.) in a 3-gallon bucket.

[0134] Preparation of Surface Treatment 6 (ST-6): A bath was prepared in a clean 3-gallon bucket by adding 47.68 g of hexafluorotitanic acid (60 wt. % in water, available from Sigma-Aldrich, St. Louis, MO) and 258.18 g of ChemDeox 395B (alkaline deoxidizer activation package commercially available from PPG Industries, Inc.) to 3 gallons of DI water.

[0135] Preparation of Surface Treatment 7 (ST-7): A bath was prepared in a clean 3-gallon bucket by adding 5% v/v of AMC257 concentrate (an acid metal cleaner commercially available from PPG Industries, Inc.) to 3 gallons of DI water.

[0136] Preparation of Surface Treatment 8 (ST-8): A bath was containing AMC66AW (an acidic deoxidizer containing sulfuric acid and zirconium and free of nitric acid commercially available from PPG Industries, Inc.) was prepared in a clean 3-gallon bucket according to manufacturer's instructions in 3 gallons of DI water.

[0137] Preparation of Pretreatment Compositions: Eight different organic-containing pretreatment compositions (PT A-H) were prepared for testing. Each pretreatment bath was built by the addition of the organic resin listed in Table 1 below and described in more detail below.

[0138] Pretreatment Composition Bath A (PT-A): To a clean 3-gallon bucket was added 1.25% solids wt. of Nupal 435 resin based on total weight of the pretreatment composition bath (an organic pretreatment containing an epoxy ester of phosphoric acid and fluoride which is commercially available from PPG Industries, Inc.) to 11.35 liters of water. The material was circulated using an immersion heater until it reached the set temperature of 80° F. before use.

[0139] Pretreatment Composition Bath B (PT-B): To a clean 3-gallon bucket was added 2.50% solids wt. of Nupal 435 resin based on total weight of the pretreatment composition bath to 11.35 liters of water. The material was circulated using an immersion heater set to 80° F. before use.

[0140] Pretreatment Composition Bath C (PT-C): To a clean 3-gallon bucket was added 5.00% solids wt. of Nupal 435 resin based on total weight of the pretreatment composition bath to 11.35 liters of water. The material was circulated using an immersion heater set to 80° F. before use.

[0141] Pretreatment Composition Bath D (PT-D): To a clean 3-gallon bucket was added 10.00% solids wt. of Nupal 435 resin based on total weight of the pretreatment bath composition to 11.35 liters of water. The material was circulated using an immersion heater set to 80° F. before use.

[0142] Pretreatment Composition Bath E (PT-E): To a clean 3-gallon bucket was added 1.25% solids wt. of Nupal 510 resin based on total weight of the pretreatment bath composition (organic pretreatment containing an epoxy ester of phosphoric acid, fluoride and fluorozirconate which is commercially available from PPG Industries, Inc.) to 11.35 liters of water. The material was circulated using an immersion heater set to 80° F. before use.

[0143] Pretreatment Composition Bath F (PT-F): To a clean 3-gallon bucket was added 2.50% solids wt. of Nupal 510 resin based on total weight of the pretreatment bath composition to 11.35 liters of water. The material was circulated using an immersion heater set to 80° F. before use.

[0144] Pretreatment Composition Bath G (PT-G): To a clean 3-gallon bucket was added 5.00% solids wt. of Nupal 510 resin based on total weight of the pretreatment bath composition to 11.35 liters of water. The material was circulated using an immersion heater set to 80° F. before use.

[0145] Pretreatment Composition Bath H (PT-H): To a clean 3-gallon bucket was added 10.00% solids wt. of Nupal 510 resin based on total weight of the pretreatment composition to 11.35 liters of water. The material was circulated using an immersion heater set to 80° F. before use.

TABLE 1

Pretreatment Compositions

Pretreatment Composition	Code	Resin Solids Nupal 435 (% wt)	Resin Solids Nupal 510 (% wt)
Bath A	PT-A	1.25	0
Bath B	PT-B	2.50	0
Bath C	PT-C	5.00	0
Bath D	PT-D	10.00	0
Bath E	PT-E	0	1.25
Bath F	PT-F	0	2.50
Bath G	PT-G	0	5.00
Bath H	PT-H	0	10.00

[0146] In the following examples, any pretreatment bath that was heated above ambient temperature was heated with an immersion heater (Polyscience Sous Vide Professional, Model #7306AC1B5, available from Polyscience, Niles, Illinois) set to low agitation mode during immersion of panels, to circulate and heat the composition contained therein. Any cleaner bath that was applied via panel immersion and was heated above ambient temperature was heated in the same manner as the pretreatment baths except the immersion heater was set to high agitation mode during panel immersion.

[0147] Electrocoats used after pretreatment and prior to corrosion testing include ED7000Z (cationic electrocoat commercially available from PPG Industries, Inc.) and EPIC 200 (cationic electrocoat commercially available from PPG Industries, Inc.), each prepared according to manufacturer's instructions.

[0148] As detailed below, panels treated according to the following examples were treated according to one of Treatment Methods A-I illustrated in Tables 2-11.

TABLE 2

Treatment Method A	
Step 1A	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2A	Deionized water rinse (30 seconds, 70° F., immersion application)
Step 3A	Deionized water rinse (30 seconds, 70° F., spray application)
Step 4A	Pretreatment (10 seconds, 80° F., immersion application)
Step 5A	Deionized water rinse (30 seconds, 70° 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, 70° F., immersion application)
Step 3B	Deionized water rinse (30 seconds, 70° F., spray application)
Step 4B	Pretreatment (30 seconds, 80° F., immersion application)
Step 5B	Deionized water rinse (30 seconds, 70° F., spray application)
Step 6B	Hot air dry (120 seconds, 140° F.)

TABLE 4

Treatment Method C	
Step 1C	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2C	Deionized water rinse (30 seconds, 70° F., immersion application)

TABLE 4-continued

Treatment Method C	
Step 3C	Deionized water rinse (30 seconds, 70° F., spray application)
Step 4C	Pretreatment (60 seconds, 80° F., immersion application)
Step 5C	Deionized water rinse (30 seconds, 70° F., spray application)
Step 6C	Hot air dry (120 seconds, 140° F.)

TABLE 5

Treatment Method D	
Step 1D	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2D	Deionized water rinse (30 seconds, 70° F., immersion application)
Step 3D	Deionized water rinse (30 seconds, 70° F., spray application)
Step 4D	Pretreatment (120 seconds, 80° F., immersion application)
Step 5D	Deionized water rinse (30 seconds, 70° F., spray application)
Step 6D	Hot air dry (120 seconds, 140° F.)

TABLE 6

Treatment Method E	
Step 1E	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2E	Deionized water rinse (30 seconds, 70° F., immersion application)
Step 3E	Deionized water rinse (30 seconds, 70° F., spray application)
Step 4E	Pretreatment (180 seconds, 80° F., immersion application)
Step 5E	Deionized water rinse (30 seconds, 70° F., spray application)
Step 6E	Hot air dry (120 seconds, 140° F.)

TABLE 7

Treatment Method F	
Step 1F	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2F	Deionized water rinse (30 seconds, 70° F., immersion application)
Step 3F	Deionized water rinse (30 seconds, 70° F., spray application)
Step 4F	Pretreatment (120 seconds, 70° F., immersion application)
Step 5F	Deionized water rinse (30 seconds, 70° F., spray application)
Step 6F	Hot air dry (120 seconds, 140° F.)

TABLE 8

Treatment Method G	
Step 1G	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2G	Deionized water rinse (30 seconds, 70° F., immersion application)
Step 3G	Deionized water rinse (30 seconds, 70° F., spray application)
Step 4G	Pretreatment (120 seconds, 90° F., immersion application)
Step 5G	Deionized water rinse (30 seconds, 70° F., spray application)
Step 6G	Hot air dry (120 seconds, 140° F.)

TABLE 9

Treatment Method H	
Step 1H	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2H	Deionized water rinse (30 seconds, 70° F., immersion application)
Step 3H	Deionized water rinse (30 seconds, 70° F., spray application)
Step 4H	Pretreatment (120 seconds, 120° F., immersion application)
Step 5H	Deionized water rinse (30 seconds, 70° F., spray application)
Step 6H	Hot air dry (120 seconds, 140° F.)

TABLE 10

Treatment Method I	
Step 1I	MEK Solvent immersion (120 seconds, 70° F., immersion application)
Step 2I	Wipe dry
Step 3I	Deionized water rinse (30 seconds, 70° F., immersion application)
Step 4I	Deionized water rinse (30 seconds, 70° F., spray application)
Step 5I	Pretreatment (120 seconds, 80° F., immersion application)
Step 6I	Deionized water rinse (30 seconds, 70° F., spray application)
Step 7I	Hot air dry (120 seconds, 140° F.)

TABLE 11

Treatment Method J	
Step 1J	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2J	Deionized water rinse (30 seconds, 70° F., immersion application)
Step 3J	Deionized water rinse (30 seconds, 70° F., spray application)
Step 4J	Acidic cleaner (120 seconds, 80° F., immersion application)
Step 5J	Deionized water rinse (30 seconds, 70° F., spray application)
Step 6J	Pretreatment (120 seconds, 80° F., immersion application)
Step 7J	Deionized water rinse (30 seconds, 70° F., spray application)
Step 8J	Hot air dry (120 seconds, 140° F.)

TABLE 12

Treatment Method K	
Step 1K	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2K	Deionized water rinse (30 seconds, 70° F., immersion application)
Step 3K	Deionized water rinse (30 seconds, 70° F., spray application)
Step 4K	Hot air dry (120 seconds, 140° F.)

[0149] Following completion of one of Treatment Methods A to K, all panels were electrocoated with either EPIC 200 (a cationic electrocoat with components commercially available from PPG) or ED7000Z (a cationic electrocoat with components commercially available from PPG). 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, Ameteck, Berwyn, Pennsylvania) was DC power supplied. The electrocoat application conditions were voltage set point of 180V-200V, a ramp time of 30 s, and a current density of 1.6 mA/cm2. The electrocoat was maintained at 90° F. The film thickness was coulomb controlled to deposit a target film thickness of 0.6±0.2 mils for ED7000Z and 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.

[0150] Electrocoated panels were scribed with a 10.2 cm vertical line in the middle of the panel down to the metal substrate. Scribed panels were exposed to either GM cyclic corrosion test GMW14872 for a minimum of nine days up to 40 days or to ASTM B117 salt spray for a minimum of one week up to 40 days. Panels for each condition were run in duplicate. The average scribe creep of two panels for each treatment combination are listed in Tables 12-16 below. Scribe creep refers to the area of paint loss around the scribe either through corrosion or disbondment (e.g.: affected paint to affected paint). A scribe creep listed as "Fail" indicates catastrophic delamination of the electrocoat layer that precludes reliable scribe creep measurements.

Example 1: Corrosion Performance on ZEK-100 Panels Alkaline Cleaned and Treated with Organic Pretreatments

[0151] ZEK-100 substrate received from POSCO was evaluated. Panels were cut to 4" by 5" size using a panel cutter. Panels were treated according to one of Treatment Methods A to H or K outlined in Tables 2 to 10 and 12 above. Specifically, panels were spray cleaned and degreased for 120 seconds at 10-15 psi in ST-1 (125° 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). Panels were then treated using one of the following pretreatment coatings: (1) PT-A to PT-D; or (2) PT-E to PT-H. Panels treated according to Treatment Method K were not treated with any pretreatment composition.

[0152] After immersion in one of PT-A to H, panels were rinsed by a deionized water spray rinse using a Melnor Rear-Trigger 7-Pattern nozzle set to shower mode (75° F.) for 30 seconds. All panels were warm air dried using a Hi-Velocity handheld blow-dryer made by Oster® (model number 078302-300-000) on high-setting at a temperature of about 50-55° C. until the panel was dry (about 1-5 minutes).

[0153] Panels then were electrocoated and exposed to corrosion testing as described above. Data are presented in Tables 13-15.

[0154] One panel was evaluated using XPS depth profiling. The XPS depth profile of the substrates were generated using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons (<5 eV) and argon ions. The binding energy axis was calibrated using sputter cleaned Cu foil (Cu 2p3/2=932.62 eV, Cu 2p3/2=75.1 eV) and Au foils (Au 4f7/2=83.96 eV). Peaks were charge referenced to CHx band in the carbon is spectra at 284.8 eV. Measurements were made at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3-6 nm (95% of the signal originated from this depth or shallower). Quantification was done using instrumental relative sensitivity factors (RSFs) that account for the x-ray cross section and inelastic mean free path of the electrons. Ion sputtering was done using 2 kV Ar+ rastered over a 2 mm×2 mm area. The sputtering rate in the Al_2O_3 layer was 9.5 nm/min. Data are reported in FIG. **1**A.

TABLE 13

ZEK-100 Scribe Creep Corrosion Results for Surface Treatment 1 → PT-C → Treatment Methods A-G → EPIC 200

Treatment Method	Average Cyclic Corrosion (15 Cycles) (mm)	Average Cyclic Corrosion (mm/day)	Salt Spray Average Days to Failure (days)	Average Salt Spray (mm/day)
A	19.9	1.33	6	2.10
B	13.3	0.89	7	1.62
C	10.7	0.71	8	1.36
D	5.1	0.34	11	0.70
E	7.1	0.47	11	0.76
F	10.3	0.69	11	0.85
G	13.6	0.91	8	1.06

TABLE 14

ZEK-100 Scribe Creep Corrosion Results for ST-1 → PT-C → Treatment Methods D, H → ED7000Z

Treatment Method	Salt Spray Average Days to Failure (days)	Average Salt Spray (mm/day)
D	11	0.77
H	13	0.55

[0155] The data in Tables 13 and 14 demonstrate that treatment of the panels according to Treatment Methods C to H resulted in improved corrosion performance compared to panels treated according to Treatment Methods A or B. Specifically, the data demonstrate that immersion times in pretreatment compositions for 60 sec to 180 sec provided similar corrosion protection and that each were better than corrosion seen on panels immersed in a pretreatment composition for either 10 sec or 30 sec. The data also demonstrate that pretreatment compositions maintained at temperatures from 70 F to 120 F provide consistent corrosion performance.

TABLE 15

ZEK-100 Scribe Creep Corrosion Results for ST-1 → PT-A to PT-H → Treatment Method D → ED7000Z

PT Condition	Average Cyclic Corrosion (8 Cycles) (mm)	Average Cyclic Corrosion (mm/day)	Average Salt Spray (7 days) (mm)	Average Salt Spray (mm/day)
A	4.72	0.59	1.30	0.19
B	2.76	0.35	1.76	0.25
C	3.53	0.44	1.57	0.22
D	5.12	0.64	4.46	0.64
E	12.82	1.60	7.15	1.02
F	3.85	0.48	1.27	0.18
G	20.63	2.58	2.43	0.35
H	33.35	4.17	18.80	2.69
NA*	16.50	2.06	13.18	1.88

*Panel treated with ST-1 only and no pretreatment

[0156] Data from panels run according to Treatment Method D (ST-1 only or ST-1 and PT-A to PT-H) are shown in Table 15. Panels cleaned with an alkaline cleaner only (ST-1) significantly underperformed compared to panels treated with ST-1 and then one of PT-A to PT-G. Additionally, these data demonstrate that corrosion resistance of panels cleaned with an alkaline cleaner and then treated with one of PT-A to PT-D had good corrosion performance.

Panels cleaned with an alkaline cleaner and then treated with PT-F and PT-G had better corrosion performance than panels cleaned and then treated with PT-E and PG-H.

Example 2—Corrosion Protection of ZEK-100 with a Multi-Step Cleaning System Followed by an Organic Pretreatment

[0157] Panels were optionally treated using an acidic Surface Treatment (one of ST-4 to ST-8) following the alkaline Surface Treatment (ST-1) and prior to the pretreatment (PT-C). These panels were electrocoated using ED7000Z and were exposed to corrosion testing as described above. Data are reported in Table 16.

[0158] One panel was evaluated using XPS depth profiling as described in Example 1 above. Data are reported in FIGS. **1**B and **1**C.

TABLE 16

ZEK-100 Scribe Creep Corrosion Results for Treatment Process J; ST-1 → ST-4, ST-5, ST-6, ST-7, or ST-8 → PT-C → ED7000Z

Surface	Cyclic Corrosion Testing			Salt Spray Testing		
Treatment Used	Cycles Survived	Average mm	Average mm/day	Days Survived	Average mm	Average mm/day
ST-4	15	12.04	0.80	<7	FAIL	FAIL
ST-5	10	6.53	0.65	<7	FAIL	FAIL
ST-6	15	9.87	0.66	12	9.33	0.78
ST-7	10	2.36	0.24	7	8.11	1.16
ST-8	11	15.56	1.41	7	13.78	1.97

[0159] The data in Table 16 demonstrate that panels cleaned with an alkaline cleaner and then treated with an acidic treatment composition (ST-4, ST-5, ST-6, ST-8) prior to immersion in an organic pretreatment composition had a negative impact on corrosion performance compared to corrosion performance seen on panels not treated with an acidic treatment composition prior to immersion in an organic pretreatment composition (ST-8; see also Table 13, Treatment Method C).

Example 3: Corrosion Performance on ZEK-100 Panels with Alternate Non-Etching Cleaning Systems and Treated with an Organic Pretreatment

[0160] Panels were optionally treated using an alkaline Surface Treatment (ST-1, 2, 3) prior to the pretreatment (PT-C). Panels that were not treated with an alkaline Surface Treatment were wiped with methyl ethyl ketone (MEK) solvent prior to the pretreatment (PT-C). These panels were electrocoated using ED7000Z.

TABLE 17

ZEK-100 Scribe Creep Corrosion Results for non-etching Surface Treatments; ST-1, ST-2, or ST-3 → PT-C → ED7000Z

Surface Treatment	Treatment Method	Salt Spray Average Days to Failure (days)	Average Salt Spray (mm/day)
None	I	11	0.80
ST-1	D	11	0.77
ST-2	D	11	1.07
ST-3	D	10	1.20

[0161] The data in Table 17 demonstrate that corrosion performance achieved with solvent-wiped panels followed by PT-C and with immersion in alkaline cleaners ST-2 and ST-3 followed by PT-C.

[0162] It will be appreciated by skilled artisans that numerous modifications and variations are possible in light of the above disclosure without departing from the broad inventive concepts described and exemplified herein. Accordingly, it is therefore to be understood that the foregoing disclosure is merely illustrative of various exemplary aspects of this application and that numerous modifications and variations can be readily made by skilled artisans which are within the spirit and scope of this application and the accompanying claims.

1. A system for treating a substrate comprising:

a cleaning composition having a pH greater than 8.5 or a solvent; and

a pretreatment composition comprising an organophosphate compound, an organophosphonate compound, or combinations thereof;

wherein the substrate comprises magnesium or a magnesium alloy.

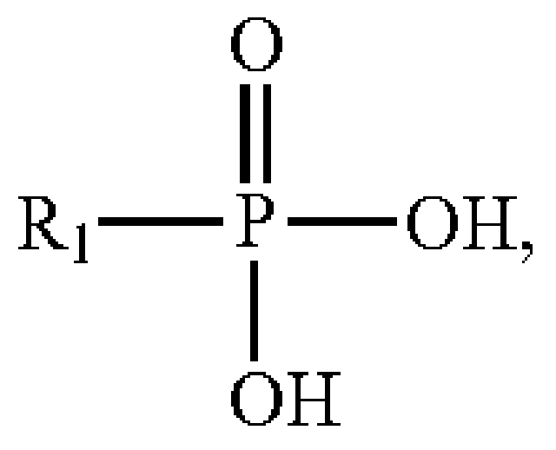
2. (canceled)

3. The system of claim **1**, wherein the pretreatment composition has a solids content of 1.25% to 25% by weight based on total weight of the pretreatment composition.

4. The system of claim **1**, wherein the organophosphate compound comprises a phosphatized epoxy.

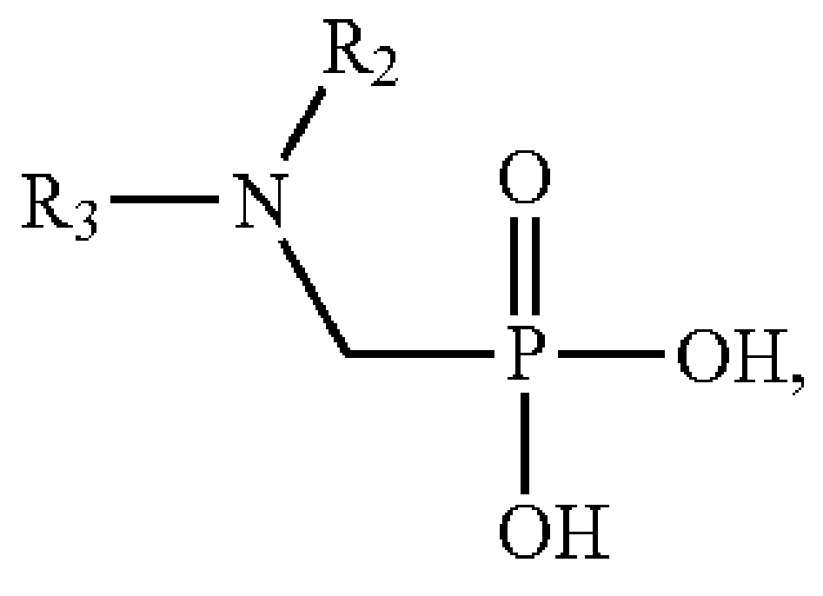
5. (canceled)

6. The system of claim **1**, wherein the organophosphonate compound comprises a phosphoric acid or a phosphonic acid comprising at least one group of the structure



wherein R_1 comprises an alkyl, an aryl, an alkoxide, an ester, and/or an ether.

7. The system of any of claims **1** to **5** claim **1**, wherein the organophosphonate compound comprises a phosphoric acid or a phosphonic acid comprising the structure



wherein R_2 comprises an alkyl, an aryl, an alkoxide, an ester, and/or an ether and R_3 comprises a hydrogen, an alkyl, an aryl, an alkoxide, an ester, an ether, and/or an epoxy.

8. The system of claim **1**, wherein the organophosphate compound and/or the organophosphonate compound are present in an amount of 1 percent by weight to 20 percent by weight based on total weight of the pretreatment composition.

9. The system of claim **1**, wherein the pretreatment composition further comprises a Group IVB metal.

10. The system of claim **9**, wherein the Group IVB metal is present in an amount of 1 ppm to 800 ppm based on total weight of the pretreatment composition.

11. The system of claim **1**, wherein the pretreatment composition further comprises free fluoride.

12. (canceled)

13. The system of claim **1**, further comprising a film-forming composition.

14. (canceled)

15. A method of treating a substrate comprising:

contacting at least a portion of a surface of the substrate with the cleaner or the solvent of the system of claim **1**; and contacting at least a portion of the surface with the pretreatment composition of claim **1**; wherein the substrate comprises magnesium or a magnesium alloy.

16. The method of claim **15**, further comprising rinsing the surface with water between contacting the substrate surface with the cleaning composition or the solvent and contacting the substrate surface with the pretreatment composition.

17. The method of claim **15**, wherein the surface is not contacted with a surface treatment composition prior to contacting with the pretreatment composition.

18. (canceled)

19. The method of claim **15**, further comprising contacting the substrate surface with the film-forming composition following the contacting with the pretreatment composition.

20. A magnesium substrate, wherein (a) oxygen and magnesium are present between an air/substrate interface and 500 nm below the air/substrate interface in a combined amount of at least 70 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; (b) carbon is present between an air/substrate interface and 500 nm below the air/substrate interface in an amount of no more than 30 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; and/or (c) fluoride is present between an air substrate interface and 500 nm below the air/substrate interface in an amount of no more than 8 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer.

21. A treated substrate, wherein at least a portion of the substrate is treated with the system of claim **1**, wherein the substrate comprises magnesium or a magnesium alloy.

22. The substrate of claim **21**, wherein (a) oxygen and magnesium are present between an air/substrate interface and 500 nm below the air/substrate interface in a combined amount of at least 70 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; (b) carbon is present between an air/substrate interface and 500 nm below the air/substrate interface in an amount of no more than 30 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer; and/or (c) fluoride is present between an air substrate interface and 500 nm below the air/substrate interface in an amount of no more than 8 atomic % as measured by XPS depth profiling using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al kα x-ray source (hv=1,486.7 eV and a concentric hemispherical analyzer.

23. The substrate of claim **21**, wherein the substrate comprises a vehicle, a part, an article, a heat exchanger, an appliance, a personal electronic device, a multi-metal article, or combinations thereof.

24. The substrate of claim **23**, wherein the vehicle comprises an automobile or an aircraft.

25. The substrate of claim **21**, wherein the substrate comprises a three-dimensional component formed by an additive manufacturing process.

26. (canceled)

* * * * *