(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 397 786 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
10.07.2024 Bulletin 2024/28

(21) Application number: **23150086.9**

(22) Date of filing: **03.01.2023**

(51) International Patent Classification (IPC):
C23C 22/34 *(2006.01)* ***C23C 22/36*** *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C23C 22/367; C23C 22/34; C23C 22/368; C23C 22/44

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

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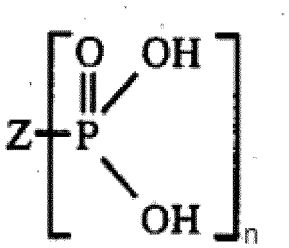
(54) **CONVERSION COATING COMPOSITION FOR COLOURED LAYERS ON ALUMINIUM**

(57) The present disclosure is directed to an aqueous conversion coating composition for the treatment of aluminium or aluminium alloys, said composition having a pH of less than 3 and comprising:
i) at least one water-soluble polyphosphonic acid or a water-soluble salt thereof, wherein said polyphosphonic acid has the general formula (I):



(I)

in which:
n is at least 2; and,
Z is a connecting organic moiety having an effective valency of n, said polyphosphonic acid being characterized in that at least two phosphonic groups are separated by a C_1-C_2 alkylene bridge which may be optionally interrupted by one or more heretoatoms selected from N or O;

ii) at least one mineral acid;
iii) at least one water-soluble or water-dispersible fluoroacid or a salt thereof, wherein said fluoroacid is defined by the following general empirical formula (II):

$$H_pT_qF_rO_s \qquad (II)$$

wherein:
each of q and r represents an integer from 1 to 10;
each of p and s represents an integer from 0 to 10; and,
T represents an element selected from the group consisting of Ti, Zr, Hf, Si, Sn, Al, Ge, and B; and,

iv) at least one tungstate salt,
wherein said composition is characterized in that it is substantially free of chromium (Cr) compounds.

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Description

FIELD OF THE INVENTION

[0001] The present invention is directed to an aqueous, acidic conversion coating composition that is characterized as being free of chromium. More particularly, the present invention is directed to an aqueous, acidic conversion coating composition comprising at least one water-soluble polyphosphonic acid and at least one tungstate salt.

BACKGROUND TO THE INVENTION

[0002] The terms "*conversion coating*" and "*conversion treatment*" refer to a treatment of the surface of a substrate which causes the surface material to be chemically converted to a different material. Typically, a metal or alloyed surface is chemically converted to provide a tightly adherent coating, all or part of which consists of a stabilized form - for instance an oxidized form - of the substrate metal. Such chemical conversion coatings can demonstrate high corrosion resistance as well as providing a strong bonding affinity for subsequent coating layers, such as paints, inks and varnishes.

[0003] Whilst aluminium (Al) protects itself against corrosion by forming an oxide coating, this protection is not complete. As such, aluminium and aluminium alloys do exhibit some surface corrosion in the presence of moisture and electrolytes. To mitigate this, there are broadly two types of conversion treatment for this metal and its alloys. The first treatment utilizes anodic oxidation - or anodization - in which the aluminum component is immersed in a chemical bath, such as a chromic or sulfuric acid bath, and an electric current is passed therethrough: the resulting conversion coating on the surface of the aluminum component offers resistance to corrosion and a bonding surface for organic finishes. The second treatment type provides a chemical conversion coating whereby a chemical solution is applied to the aluminium component - through immersion, manual application, spraying or the like - without the passage of an electric current in the process. The present disclosure is directed to this second treatment type.

[0004] Prior art chemical conversion compositions have predominantly been based upon acidic aqueous solutions of chromate salts. Upon applying an acidic chromate solution to an aluminium or aluminium alloy substrate, surface aluminium atoms are oxidized to form, in effect, an interfacial layer of hydrated basic chromium chromate ($Cr_2O_3CrO_3 . xH_2O$) and hydrous oxides of both chromium and aluminium. As the acid is consumed in the oxidation reaction, however, the pH at the surface-liquid interface increases: this diminishes the combining power of chromium in the aqueous phase and leads to the precipitation of a thin gelatinous film comprising chromium hydroxide and complexes of chromium ions and aluminium. This film builds up until acid protons can no longer contact the aluminium metal and the surface redox reactions are thereby stopped: the resulting gel-like film may then be permitted to harden.

[0005] Anteriorly, hexavalent chromium (Cr^{6+} or chromium(VI)) was used in such compositions to supply the chromium present in the conversion coating. US Patent No. 2,796,370 (Ostrander), for example, provided a composition for use in the application of a chemically bonded coating on *inter alia* aluminium surfaces, said composition consisting essentially of hexavalent chromium, a fluorine bearing compound and a soluble cyanide selected from the group consisting of ferricyanide and ferrocyanide. However, the toxicological properties of chromium(VI) are problematic and the use of chromium(VI)-containing passivation treatments has been strongly limited by *inter alia* EC directive 2000/53/EC. Consequently, there has been some focus in the art on the treatment of aluminium surfaces with compositions in which the chromium is at least partly in the trivalent state: mention in this regard may be made of the disclosures of: US Patent No. 4,578,122 A (Crotty); US Patent No. 10,156,016 B2 (Kramer et al.); US Patent No. 5,304,257 A (Pearlstein et al.); and, US 7,029,541 B2 (Diaddario et al.). The Cr(III), as used in these citations, is not toxic and the concomitant waste removal of Cr(III) is not as expensive as that of hexavalent chromium. However, despite this advantage, certain authors have elected to focus on conversion coating compositions which do not contain chromium at all.

[0006] US Patent No. 5,468,307 A (Schriever) describes an aqueous chemical bath for producing an oxide-film cobalt conversion coating on an aluminium or aluminium alloy substrate, said chemical bath being prepared by reacting: (a) in the presence of an oxidizer; (b) a cobalt (II) salt of which the counter anion is chloride, bromide, nitrate, cyanide, thiocyanate, phosphate, sulphate, acetate or carbonate; (c) a nitrate salt of lithium, potassium, sodium, calcium or magnesium; and, (d) ammonium acetate, wherein: i) the concentration of said cobalt (II) salt is from 0.01 moles per liter to the saturation limit of the final solution; ii) the concentration of said metal nitrate salt is from 0.03 to 2.5 moles per liter of final solution; and, iii) the concentration of said ammonium acetate is from 0.06 to 6.0 moles per liter of final solution. The presence of nitrate salts in this composition is considered disadvantageous. Such salts are converted to NO_x during the spontaneous decomposition or the intended oxidation activity, and this NO_x diffuses into the atmosphere as a pollutant.

[0007] U.S. Pat. No. 6,328,874 (Kinlen et al.) discloses a method for protecting an aluminum surface from corrosion comprising, contacting the aluminum surface with a mixture of water, a multifunctional polymeric organic acid and a monomer of an intrinsically conductive polymer and imposing an electrical potential between the aluminum surface as the anode and a cathode, where the electrical potential is sufficient to polymerize the monomer of the intrinsically conductive polymer and to form aluminum oxide, thereby forming on the aluminum surface a coating of the multifunctional

polymeric organic acid salt of the intrinsically conductive polymer intermixed with aluminum oxide.

[0008] US Patent No. 6,419,731 (Inbe et al.) describes a non-chromate rust preventive agent for aluminum which comprises: a zirconium compound in an amount of 100 to 100000 ppm as zirconium ion; a fluoride ion in an amount of 125-125000 ppm; a water-soluble resin in an amount of 100 to 100000 ppm on a nonvolatile matter basis; and, an aluminum salt in an amount of 10 to 10000 ppm as aluminum ion, wherein said water-soluble resin has a functional group selected from the group consisting of carboxyl, hydroxyl, a sulfo and amino groups, which forms a bond with the zirconium compound, aluminum, or both, in film formation.

[0009] US Patent No. 9,476,125 B2 (Cano-Iranzo et al.) describes a conversion coating for the treatment of metallic surfaces, the coating comprising a conducting polymer dispersion containing one or more silanes, and an inorganic metallic salt of at least one of molybdenum, magnesium, zirconium, titanium, vanadium, cerium, hafnium, silicon, aluminum, boron, cobalt and zinc, wherein the concentration of the inorganic metallic salt is between 2.0 g/L (grams per liter) and 20 g/L (grams per liter) and the pH of the coating is between 1 and 6.0.

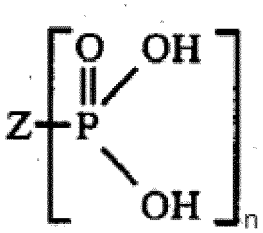
[0010] Despite the developments of the prior art, it is submitted that non-chromate type treatments are rarely as effective as chromate type conversion coatings in providing practicable corrosion resistance for aluminium and aluminium alloy substrates. A contributory reason for this is considered to be the difficulty in assessing coating development during the application of the conversion coating: whereas chromate coatings tend to provide an observable yellow-brownish color on aluminium substrates, by which coating coverage can be visually assessed by an artisan, many known non-chromate conversion coatings tend to be colorless, transparent, poorly visible or indistinct.

[0011] The present disclosure therefore seeks to provide a chromium-free conversion coating which affords effective corrosion resistance to aluminium and aluminium alloy substrates, which is a commercially viable alternative to known coatings, which is facile to apply and for which the application method can be visually monitored - and thereby easily modified and optimized - to ensure a uniform conversion coating.

STATEMENT OF THE INVENTION

[0012] In accordance with a first aspect of the disclosure, there is provided an aqueous conversion coating composition for the treatment of aluminium or aluminium alloys, said composition having a pH of less than 3 and comprising:

i) at least one water-soluble polyphosphonic acid or a water-soluble salt thereof, wherein said polyphosphonic acid has the general formula (I):



(I)

in which:

n is at least 2; and,
Z is a connecting organic moiety having an effective valency of n, said polyphosphonic acid being characterized in that at least two phosphonic groups are separated by a C_1-C_2 alkylene bridge which may be optionally interrupted by one or more heretoatoms selected from Nor O;

ii) at least one mineral acid;
iii) at least one water-soluble or water-dispersible fluoroacid or a salt thereof, wherein said fluoroacid is defined by the following general empirical formula (II):

$$H_pT_qF_rO_s \qquad (II)$$

wherein:

each of q and r represents an integer from 1 to 10;
each of p and s represents an integer from 0 to 10; and,
T represents an element selected from the group consisting of Ti, Zr, Hf, Si, Sn, Al, Ge, and B; and,

iv) at least one tungstate salt,

wherein said composition is characterized in that it is substantially free of chromium (Cr) compounds. The composition may desirably also be substantially free of nitrate compounds.

[0013] In an important embodiment, the composition has a pH of from 1 to 3 and comprises, based on the weight of the composition:

from 25 to 80 wt.%, preferably from 40 to 80 wt.% of water;
from 5 to 25 wt.%, preferably from 5 to 20 wt.% of i) said at least one water-soluble polyphosphonic acid or a water-soluble salt thereof;
from 5 to 50 wt.%, preferably from 5 to 30 wt.% of ii) said at least one mineral acid;
from 5 to 35 wt.%, preferably from 5 to 25 wt.% of iii) said at least one water-soluble or water-dispersible fluoroacid or a salt thereof; and,
from 1 to 5 wt.%, preferably from 1 to 4 wt.% of iv) said at least one tungstate salt.

[0014] In certain embodiments, it is preferred that component iv) said at least one tungstate salt is selected from the group consisting of: lithium orthotungstate (Li_2WO_4); sodium orthotungstate (Na_2WO_4); potassium orthotungstate (K_2WO_4); ammonium orthotungstate ($(NH_4)_2WO_4$); ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}$); potassium metatungstate ($K_6H_2W_{12}O_{40}$); and, sodium metatungstate ($Na_6H_2W_{12}O_{40}$). For example, component iv) said at least one tungstate salt may be selected from the group consisting of: sodium orthotungstate (Na_2WO_4); sodium metatungstate ($Na_6H_2W_{12}O_{40}$); potassium orthotungstate (K_2WO_4); and, potassium metatungstate ($K_6H_2W_{12}O_{40}$).

[0015] In accordance with a second aspect of the disclosure, there is provided a process for imparting a conversion coating to an aluminium or aluminium alloy substrate, said process comprising contacting at least one surface of the substrate with an aqueous composition as defined herein above and in the appended claims at a temperature ranging from 20° C to 90° C for a period of time sufficient to form a coating thereon. As the coating is formed on the aluminium or aluminium alloy substrate, it possesses a bluish color which is visible to the artisan: by visual inspection, the artisan can assess the coverage of coating.

[0016] In accordance with a third aspect of the disclosure, there is provided a coated substrate obtained by the process defined herein above and in the appended claims. As documented in the Examples below, the coated substrates provide effective corrosion resistance. Moreover, the coatings have a microcrystalline structure which provides an effective surface for the subsequent adhesion of varnishes, inks or paints, which paints may be provided in solvent-borne form, water-borne form or as powder coatings.

DEFINITIONS

[0017] As used herein, the singular forms "*a*", "*an*" and "*the*" include plural referents unless the context clearly dictates otherwise.

[0018] The terms "*comprising*", "*comprises*" and "*comprised* of" as used herein are synonymous with "*including*", "*includes*", "*containing*" or "*contains*", and are inclusive or open-ended and do not exclude additional, nonrecited members, elements or method steps. If used, the phrase "*consisting of*" is closed, and excludes all additional elements. Further, the phrase *"consisting essentially of'* excludes additional material elements, but allows the inclusions of non-material elements that do not substantially change the nature of the invention.

[0019] When amounts, concentrations, dimensions and other parameters are expressed in the form of a range, a preferable range, an upper limit value, a lower limit value or preferable upper and limit values, it should be understood that any ranges obtainable by combining any upper limit or preferable value with any lower limit or preferable value are also specifically disclosed, irrespective of whether the obtained ranges are clearly mentioned in the context.

[0020] The words *"preferred*", "*preferably*", "*particularly*" and "*desirably*" are used frequently herein to refer to embodiments of the disclosure that may afford particular benefits, under certain circumstances. However, the recitation of one or more preferable, preferred, particular or desirable embodiments does not imply that other embodiments are not useful and is not intended to exclude those other embodiments from the scope of the disclosure.

[0021] As used throughout this application, the word "*may*" is used in a permissive sense - that is meaning to have the potential to - rather than in the mandatory sense.

[0022] The present compositions are defined herein as being "*substantially free*" of certain compounds, elements, ions or other like components. The term "*substantially free*" is intended to mean that the compound, element, ion or other like component is not deliberately added to the composition and is present, at most, in only trace amounts which will have no (adverse) affect on the desired properties of the coating. The term "*substantially free*" encompasses those embodiments where the specified compound, element, ion, or other like component is completely absent from the composition or is not present in any amount measurable by techniques generally used in the art.

[0023] As used herein, room temperature is 23°C plus or minus 2°C.

[0024] As defined herein, the term "*conversion coating*" or "*conversion treatment*," refers to a treatment of the surface of a substrate which causes the surface material to be chemically converted to a different material. The term "*passivation*" refers to a treatment of the surface of a substrate to form a barrier layer to corrosive conditions on said surface but without a cohesive film forming a chemical bond between the surface and the passivation layer.

[0025] The term "*conversion coating composition*" as used herein refers to that composition which actually contacts the aluminium or aluminium alloy substrate. As is known in the art, such contacting typically occurs in a so-called "*bath*" which is shaped, sized and disposed to enable at least part of the substrate to be immersed therein. The bath should moreover be sized to allow for movement of the composition around and throughout the loaded substrate, which movement can be further enhanced with recirculation and / or ultrasonics. The pH of the composition within the bath, the temperature of the bath, and contact time of the substrate are result effective variables which should be monitored either manually or automatically, whenever possible.

[0026] Viscosities of the conversion coating compositions may be determined using the Brookfield Viscometer, Model RVT at standard conditions of 20°C. and 50% Relative Humidity (RH). The viscometer is calibrated using silicone oils of known viscosities, which vary from 5,000 cps to 50,000 cps. A set of RV spindles that attach to the viscometer are used for the calibration. Measurements of the conversion coating compositions are done using the No. 6 spindle at a speed of 20 revolutions per minute for 1 minute until the viscometer equilibrates. The viscosity corresponding to the equilibrium reading is then calculated using the calibration.

[0027] Unless otherwise stated, where a molar ratio is given herein with respect "*to metal* ", this refers to the total content of metal in the composition, independent of the oxidation state(s) of that metal.

[0028] As used herein, the term "*alloy*" refers to a substance composed of two or more metals or of a metal and a non-metal which have been intimately united, usually by being fused together and dissolved in each other when molten. The term "*aluminium alloy*" therefore denotes an alloy of which aluminium metal is a constituent component, which aluminium will generally comprise at least 50 wt.% - more typically at least 65 wt.% or at least 80 wt.% - of the alloy, on a metals basis. Metals which may be alloyed with aluminium include, but are not limited to, silicon, copper, zinc, magnesium, manganese, lithium, titanium, nickel, iron and bismuth.

[0029] Exemplary aluminium alloys include but are not limited to Al/Mg, Al/Si, Al/Mg/Si, Al/Zn/Mg, Al/Cu/Mg and Al/Zn/Mg/Cu of which the aluminium content is at least 90 wt.% on a metals basis. Where present in these exemplary alloys, it is preferred that, on a metals basis: the magnesium (Mg) content is at most 10 wt.%; the silicon (Si) content is at most 10 wt.%; the zinc (Zn) content is at most 5 wt.%; and, the copper (Cu) content is at most 2 wt.%.

[0030] As used herein, "*mineral acid*" refers to an acid derived from one or more inorganic compounds. A mineral acid is not organic and all mineral acids release hydrogen ions when dissolved in water.

[0031] As used herein, "*phosphoric acid*" refers to ortho-phosphoric acid having the formula H_3PO_4, which acid is typically available as an aqueous solution having a concentration up to 75 wt.% H_3PO_4. As used herein "*phosphonic acid*" refers to the phosphorus oxoacid having the formula H_3PO_3 that consists of a single pentavalent phosphorus covalently bound via single bonds to a single hydrogen and two hydroxy groups and via a double bond to an oxygen.

[0032] As used herein, the term "*α-hydroxycarboxylic acid*" means a carboxylic acid having at least one hydroxyl functional group occupying an α-position on said acid (carbon adjacent to a carboxylic acid functional group). The presence of hydroxyl groups occupying positions in the molecule other than the α-position on said acid is not precluded. When present, α-hydroxycarboxylic acid is included in the present composition in the form of the free acid.

[0033] The term "*hydrocarbyl group*" is used herein in its ordinary sense, which is well-known to those skilled in the art.

[0034] As used herein, "*C_1-C_n alkyl*" group refers to a monovalent group that contains 1 to n carbons atoms, that is a radical of an alkane and includes straight-chain and branched organic groups. As such, a "*C_1-C_4 alkyl*" group refers to a monovalent group that contains from 1 to 4 carbons atoms, that is a radical of an alkane and includes straight-chain and branched organic groups. Examples of alkyl groups include, but are not limited to: methyl; ethyl; propyl; isopropyl; n-butyl; isobutyl; sec-butyl; and, tert-butyl. In the present invention, such alkyl groups may be unsubstituted or may be substituted with one or more halogen. Where applicable for a given moiety (R), a tolerance for one or more non-halogen substituents within an alkyl group will be noted in the specification.

[0035] The terms "*alkylene group*" refers to a group that are radicals of a linear, branched or cyclic alkane, which group may be substituted or unsubstituted and may optionally be interrupted by at least one heteroatom.

[0036] As used herein, "*C_2-C_6 alkenyl*" group refers to an aliphatic carbon group that contains 2 to 6 carbon atoms and at least one double bond disposed in any position. The alkenyl group can be straight chained, branched or cyclic and may optionally be substituted with one or more halogen. Where applicable for a given moiety (R), a tolerance for one or more non-halogen substituents within an alkenyl group will be noted in the specification. The term "*alkenyl*" also encompasses radicals having "cis" and "trans" configurations, or alternatively, "E" and "Z" configurations, as appreciated by those of ordinary skill in the art. In general, however, a preference for unsubstituted alkenyl groups containing from 2 to 6 (C_2-C_6) or from 2 to 4 (C_2-C_4) carbon atoms should be noted. And Examples of C_2-C_6 alkenyl groups include, but are not limited to: ethenyl; 1-propenyl; 2-propenyl; 1-methyl-ethenyl; 1-butenyl; 2-butenyl; 4-methylbutenyl; 1-pentenyl;

2-pentenyl; 3-pentenyl; 4-pentenyl; 4-methyl-3-pentenyl; 1-hexenyl; 3-hexenyl; and, 5-hexenyl.

[0037] The term "*C_3-C_6 cycloalkyl*" as used herein means an optionally substituted, saturated cyclic hydrocarbon having 3-6 carbon atoms. In the present invention, such cycloalkyl groups may be unsubstituted or may be substituted with one or more halogen. Where applicable for a given moiety (R), a tolerance for one or more non-halogen substituents within a cycloalkyl group will be noted in the specification. Exemplary cycloalkyl groups include cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl groups.

[0038] As used herein, an "*C_6-C_{10} aryl*" group used alone or as part of a larger moiety - as in "*aralkyl group*" - refers to monocyclic, bicyclic and tricyclic ring systems in which the monocyclic ring system is aromatic or at least one of the rings in a bicyclic or tricyclic ring system is aromatic. The bicyclic and tricyclic ring systems include benzofused 2-3 membered carbocyclic rings. In the present invention, such aryl groups may be unsubstituted or may be substituted with one or more halogen. Where applicable for a given moiety (R), a tolerance for one or more non-halogen substituents within an aryl group will be noted in the specification. Exemplary aryl groups include phenyl or naphthyl, or substituted phenyl or substituted naphthyl.

[0039] An "*alkoxy group*" refers to a monovalent group represented by -OA where A is an alkyl group: non-limiting examples thereof are a methoxy group, an ethoxy group and an iso-propyloxy group.

[0040] The term "*substituted*" refers to substitution with at least one suitable substituent. For completeness: the substituents may connect to the specified group or moiety at one or more positions; and, multiple degrees of substitution are allowed unless otherwise stated. Further, the terms "*substitution*" or "*substituted with*" include the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound that does not spontaneously undergo transformation by, for instance, rearrangement, cyclization or elimination.

[0041] Having regard to the α-hydroxycarboxylic acid defined above and hereinbelow, substitution(s) of the group R_1 will conventionally be selected from the group consisting of: halogen; oxo; -OH; and, -COOH.

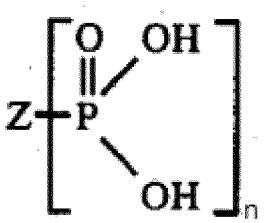
[0042] Where mentioned, the expression "*interrupted by at least one heteroatom*" means that the main chain of a residue comprises, as a chain member, at least one atom that differs from carbon atom. More particularly the term "*heteroatom*" refers to nitrogen, oxygen, halogens, phosphorus or sulfur. Oxygen (O) and nitrogen (N) may be mentioned as typical heteroatoms in the context of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0043] The composition comprises by necessity acidic components. *In toto* the added amount of the acidic components is that required to adjust the pH of the conversion coating composition to a value of less than 3, in particular to a pH of from 1.0 to 3.0 or from 1.5 to 3.0.

Component (i)

[0044] A first required component of the composition of the present invention is constituted by at least one water-soluble polyphosphonic acid or a water-soluble salt thereof, wherein said polyphosphonic acid has the general formula (I):



(I)

in which:

n is at least 2; and,
Z is a connecting organic moiety having an effective valency of n,

said polyphosphonic acid being characterized in that at least two phosphonic groups are separated by an alkylene bridge having 1 or 2 carbon atoms (*C_1-C_2 alkylene*). It is re-iterated that the C_1-C_2 alkylene bridge may optionally be interrupted by at least one heteroatom selected from O or N.

[0045] In particular embodiments, n is an integer from 2 to 5 or, preferably, either 2 or 3. Most desirably, said polyphosphonic acid is selected from a group consisting of aminotris(methylene phosphonic acid) (ATMP); 1-hydroxyethylidene-

1,1-diphosphonic acid (HEDP); hexamethylene diamine tetra(methylene phosphonic acid) (HDTMP); diethylenetriamine penta(methylenephosphonic acid) (DTPMP); and, mixtures thereof. A particular preference for the use of 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) should be noted.

[0046] Suitable water soluble salts of the aforementioned polyphosphonic acids include the sodium, potassium, calcium, magnesium, ammonium, triethanolammonium, diethanolammonium and monoethanolammonium salts.

[0047] In total, the polyphosphonic acids or the water soluble salts thereof are preferably included in the compositions in an amount of from 5 to 25 wt.%, for example from 5 to 20 wt.%, based on the weight of the composition.

Component (ii)

[0048] The conversion coating compositions of the present invention comprise at least one mineral acid. The use of nitric acid is not precluded but is not preferred; conversely, the addition of at least one of phosphoric acid, phosphonic acid, sulphurous acid, sulphuric acid, hydrochloric acid and hydrobromic acid is considered to be particularly suitable. A particular preference for the use of at least one of phosphoric acid, phosphonic acid, sulphurous acid and sulphuric acid may be mentioned. And in an important embodiment, the mineral acid of the composition in constituted by phosphoric acid.

[0049] The above recited pH of the conversion coating composition is somewhat determinative of the added amount of such acid(s). Within that pH constraint, the conversion coating composition may comprise from 5 to 50 wt.%, for example from 5 to 30 wt.% of mineral acid.

[0050] In that embodiment where the mineral acid comprises or consists of phosphoric acid, it is preferred that the molar ratio of phosphonate groups to H_3PO_4 in the conversion coating composition is in the range from 2:1 to 1:1, more preferably in the range from 1.75: 1 to 1.25: 1 and most preferably from 1.6: 1 to 1.4: 1. Compositions meeting these molar ratio conditions have been found to be effective and stable without promoting substantial etching of the aluminium or aluminium alloy substrates to which they are applied.

Component (iii)

[0051] In accordance with the present invention, the conversion coating composition comprises at least one water-soluble or water-dispersible fluoroacid or a salt thereof, wherein said fluoroacid is defined by the following general empirical formula (II):

$$H_pT_qF_rO_s \qquad (II)$$

wherein:

each of q and r represents an integer from 1 to 10;
each of p and s represents an integer from 0 to 10; and,
T represents an element selected from the group consisting of Ti, Zr, Hf, Si, Sn, Al, Ge, and B.

Preferred fluoroacids of empirical formula (II) include compounds where: T is selected from Ti, Zr, or Si; p is 1 or 2; q is 1; r is 2, 3, 4, 5 or 6; and, s is 0, 1, or 2.

[0052] Exemplary fluoroacids used in the process of the invention may be selected from the group consisting of: fluorotitanic acid (H_2TiF_6); fluorozirconic acid (H_2ZrF_6); fluorosilicic acid (H_2SiF_6); fluoroboric acid (HBF_4); fluorostannic acid (H_2SnF_6); fluorogermanic acid (H_2GeF_6); fluorohafnic acid (H_2HfF_6); and, fluoroaluminic acid (H_3AlF_6). Preferred fluoroacids are: fluorotitanic acid (H_2TiF_6) and fluorozirconic acid (H_2ZrF_6).

[0053] Subject to the condition that the salt is water-soluble or water dispersible, one or more of the H atoms of the aforementioned fluoroacids may be replaced by suitable cations, such as ammonium, alkaline earth metal cations or alkali metal cations. The salts of alkali metal cations and ammonium are preferred in this context and mention may therefore be made of the following examples of suitable fluoroacid salts: $(NH_4)_2ZrF_6$; $H(NH_4)ZrF_6$; $(NH_4)_2TiF_6$; $H(NH_4)_2TiF_6$; Na_2ZrF_6; K_2ZrF_6; Li_2ZrF_6; Na_2TiF_6; K_2TiF_6; and, Li_2TiF_6.

[0054] Such salts may be added directly to the composition or may be produced *in situ* in the aqueous conversion coating composition by the partial or full neutralization of the acid fluoride or acid oxyfluoride with an appropriate base. It is noted that said base may be organic or inorganic in character: ammonium bicarbonate and hydroxylamine might be used, for instance.

[0055] The fluoroacid or salt thereof is typically included in the composition such that the molar ratio of mineral acid to the metal (T) of said fluoroacid is in the range from 10:1 to 2:1, preferably from 9: 1 to 3:1 and more preferably 8: 1 to 4:1. When the level of mineral acid is outside the above ranges, the stability of the formulation is diminished: at lower levels of mineral acid within the stated ranges, the concomitant loss of stability of the formulation can be mitigated by

increasing the amount of divalent metal cations in the composition. When the level of metal (T) falls below the stated molar ranges, the stability of the composition may be substantively affected but a decline in performance in the neutral salt spray (NSS) may be observed.

[0056] In an alternative but not mutually exclusive expression, the total amount of fluoroacid or salt thereof which should be included in the conversion coating composition is from 5 to 35 wt.%, for example from 5 to 25 wt.%, based on the weight of the composition.

Component (iv)

[0057] The conversion coating composition of the present disclosure comprises a source of tungstate ions. More particularly, the conversion coating composition comprises iv) at least one tungstate salt. In certain embodiments, the composition comprises in total from 1 to 5 wt.% or from 1 to 4 wt.%, based on the weight of the composition, of tungstate salt(s).

[0058] For completeness, the term "*tungstate salt*" refers to a salt possessing: an oxoanion of tungsten or a mixed oxide of tungsten; and, a cationic moiety. Exemplary anions include but are not limited to: WO_4^{2-}(orthotungstate); HWO_4^- (hydrogentungstate); polymeric $W_2O_7^{2-}$ anions; $[W_7O_{24}]^{6-}$ (paratungstate A); $[W_{10}O_{32}]^{4-}$ (tungstate Y); $[H_2W_{12}O_{42}]^{10-}$ (paratungstate B); α-$[H_2W_{12}O_{40}]^{6-}$ (metatungstate); and, β-$[H_2W_{12}O_{40}]^{6-}$ (tungstate X), and mixtures thereof. Exemplary cations include but are not limited to: litihium (Li^+); potassium (K^+); sodium (Na^+); ammonium ($NH4^+$); magnesium (Mg^{2+}); calcium (Ca^{2+}); strontium (Sr^{2+}); barium (Ba^{2+}); and, cerium (Ce^{3+}, Ce^{4+}).

[0059] In an embodiment, the at least one tungstate salt is selected from the group consisting of: lithium orthotungstate (Li_2WO_4); sodium orthotungstate (Na_2WO_4); potassium orthotungstate (K_2WO_4); ammonium orthotungstate ($(NH_4)_2WO_4$); ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}$); potassium metatungstate ($K_6H_2W_{12}O_{40}$); and, sodium metatungstate ($Na_6H_2W_{12}O_{40}$). For example, the at least one tungstate salt may be selected from the group consisting of: sodium orthotungstate (Na_2WO_4); sodium metatungstate ($Na_6H_2W_{12}O_{40}$); potassium orthotungstate (K_2WO_4); and, potassium metatungstate ($K_6H_2W_{12}O_{40}$). The addition of sodium orthotungstate to the conversion coating composition - either as the sole tungstate salt or in combination with further tungstate salts - is particularly preferred.

Adjunct Ingredients

[0060] The present compositions may further comprise additives which are conventional in this field; in particular, the compositions might comprise: corrosion inhibitors, such as dialkylthioureas, cupric sulphate and copper sulphate; waxes; adhesion promoters; wetting agents; de-foaming agents; sequestrants; lubricants; and, mixtures thereof. As further exemplary corrosion inhibitors mention may be made of the following commercial materials: the Rodine® series, available from JMN Specialties, Inc. and Henkel Corporation; the Dodicor® series, available from Clariant AG; and, the Armohib® series available from Akzo Nobel Surfactants LLC. That aside, any such additives are necessarily minor ingredients of the present compositions and, when used, should only be used in amounts which are not deleterious to the performance of the composition and the coating derived there from.

[0061] The composition of the present invention may, in certain embodiments, comprise wax. When present, the composition may comprise up to 5 wt.% of said wax, for example from 1 to 5 wt.%, based on the weight of the composition.

[0062] Without intention to limit the present disclosure, exemplary waxes include: paraffin wax [CAS No. 8002-74-2]; polyethylene wax [CAS No. 9002-88-4]; polyethylene-polypropylene waxes; co-polymeric polyethylene waxes, for example copolymers of ethylene with at least one monomer selected from (meth)acrylic acid, maleic anhydride, vinyl acetate and vinyl alcohol, which copolymers are available under, for instance CAS Nos. 38531-18-9, 104912-80-3 and 219843-86-4; polybutene waxes; Fischer-Tropsch waxes; oxidized waxes, for example oxidized polyethylene wax [CAS No. 68441-17-8]; polar modified polypropylene waxes; microcrystalline waxes, for example microcrystalline paraffin waxes [CAS No. 63231-60-7]; montan wax and montan wax raffinates; montanic acids and salts and esters thereof; fatty acid amides such as erucamide [CAS No. 112-84-5], oleamide [CAS No. 301-02-0] and 1,2-ethylenebis(stearamide) [CAS No. 110-30-5]; and, carnauba wax.

[0063] It is preferred that any waxes included in the present composition meet at least one of the following conditions: i) an acid number of less than 200 mg KOH/g, preferably less than 100 mg KOH/g; ii) a melting point of from 40 to 200°C, preferably from 60 to 180°C; and, iii) a number average molecular weight (Mn) of at least 200 g/mol, preferably at least 400 g/mol. For completeness, these conditions are not intended to be mutually exclusive: waxes may meet one, two or three of these conditions.

[0064] A particular preference may be noted for the use of at least one wax selected from polyethylene waxes, oxidized polyethylene waxes, polypropylene waxes, oxidized polypropylene waxes or co-polymeric waxes based on ethylene or propylene as the main monomers, wherein said at least one wax is further characterized by a number average molecular weight (Mn) of from 400 to 30 000 g/mol, preferably from 1000 to 25 000 g/mol.

[0065] To facilitate their inclusion in the compositions of the present invention, waxes should be provided: i) in finely

divided powder form, in particular in a micronized form characterized by a mean particle size of less than 20 microns, as measured by laser diffraction; and / or; ii) as an aqueous dispersion, the particles of which dispersion may desirably be characterized by a mean particle size of less than 1 micron, for instance less from 20 to 500 nm, as measured by dynamic liqht scattering.

[0066] In addition to component iii) above, the presence of other complex fluoride anions in the passivation composition is not precluded and mention in this regard may be made of: fluoroindates (e.g. InF_4^{-1}); fluorophosphates (e.g. PF_6^{-1}); fluoroarsenates (e.g. AsF_6^{-1}); fluoroantimonates (e.g. SbF_6^{-1}); fluorobismuthates (e.g. BiF_6^{-1}); fluoro sulfates (e.g. SF_6^{-2}); fluoroselenates (e.g. SeF_6^{-2}); fluorotellurates (e.g. TeF_6^{-2} or $TeOF_5^{-1}$); fluorocuprates (e.g. CuF_3^{-1}); fluoroargentates; fluorozincates (e.g., ZnF_4^{-2}); fluorovanadates (e.g. VF_7^{-2}); fluoroniobates (e.g. NbF_7^{-2}); fluorotantalates (e.g. TaF_7^{-2}); fluoromolybdates (e.g. MoF_6^{-3}); fluorotungstates (e.g. WF_6^{-1}); fluoroyttrates (e.g. YF_6^{-3}); fluorolanthanates (e.g. LaF_6^{-3}); fluorocerates (e.g. CeF_6^{-3} or CeF_6^{-2}); fluoromanganates (e.g. MnF_6^{-2}); fluoroferrates (e.g. FeF_6^{-3}); fluoronickelates; and fluorocobaltates. Such anions may be included in the form of water-soluble or water dispersible salts, in particular the ammonium, alkaline earth metal or alkali metal salts.

[0067] When present, said complex fluoride anions should be included in the composition in an amount up to 0.1 moles/litres, for example up to 0.05 moles/litre.

[0068] The presence in the conversion coating composition of free fluoride ions - not bound in complex form - is also not precluded as the fluoride anions can act as accelerators in the formation of the coatings and are present at the interface between the conversion coating and the metal matrix. Such free fluoride anions can be included through the addition to the coating compositions of, for example: hydrofluoric acid; alkali metal fluorides, such as sodium fluoride; alkali metal hydrogen fluorides, such as sodium hydrogen fluoride; ammonium fluoride; and, ammonium hydrogen fluoride.

[0069] The conversion coating composition may optionally include up to 5 wt.%, for example from 1 to 3 wt.%, of non-ionic surfactants, based on the weight of the composition. Whilst other non-ionic surfactants may be have utility in the present invention, a particular preference for the use of fatty alcohol ethoxylates may be mentioned, of which examples include ethoxylated lauryl alcohol, stearyl alcohol, behenyl alcohol and oleyl cetyl alcohol.

[0070] The composition of the present invention may optionally comprise at least one α-hydroxycarboxylic acid represented by the general formula (III): $R_1CH(OH)COOH$ (III) wherein: R_1 represents a hydrogen atom, a C_1-C_4 alkyl group, a C_2-C_6 alkenyl group, a C_1-C_6 alkoxy group, a C_3-C_6 cycloalkyl group or a C_6-C_{10} aryl group.

[0071] Suitable α-hydroxycarboxylic acids include but are not limited to: glycolic acid; lactic acid (2-hydroxypropanoic acid); 2-hydroxybutanoic acid; 2-hydroxypentanoic acid; 2-hydroxyhexanoic acid; glucuronic acid; citric acid; mandelic acid; galacturonic acid; ribonic acid (2,3,4,5-tetrahydroxypentanoic acid); gluconic acid (2S,3S,4R,5S)-2,3,4,5,6-pentahydroxyhexanoic acid; tartronic acid; tartaric acid; and, malic acid.

[0072] In an embodiment, said at least one α-hydroxycarboxylic acid is selected from the group consisting of: glycolic acid; gluconic acid; lactic acid (2-hydroxypropanoic acid); 2-hydroxybutanoic acid; 2-hydroxypentanoic acid; and, 2-hydroxyhexanoic acid. More particularly, the α-hydroxycarboxylic acid(s) of the coating composition should comprise or consist of gluconic acid.

[0073] For completeness, it is again noted that the above recited pH of the conversion coating composition is somewhat determinative of the added amount of such α-hydroxycarboxylic acid(s). When added within that pH constraint, the α-hydroxycarboxylic acid(s) should conventionally be included in the aqueous conversion coating composition in an amount up to 0.1 moles/litres, for example up to 0.05 moles/litre.

[0074] It is considered that the corrosion-protection performance of the disclosed conversion coating compositions - and resulting passivate coatings - can be enhanced by the incorporation of a transition metal salt and / or a transition metal complex therein. Considered particularly useful in this regard are the salts or complexes of transition metals selected from the group consisting of Ce, Ni, Co, V, Fe, Zn, Zr, Mn, Mo, Zr, Hf, Bi and the lanthanides.

[0075] Whilst said transition metals may be present in the complex fluoride anions mentioned hereinabove, such transition metals may alternatively or additionally be included in the composition as complexes with other ligands and / or as salts with further anions, provided said salts are at least partially soluble in water. As examples of anions, there may be mentioned: oxide; hydroxide; sulphate; chloride; iodide; citrate; lactate; succinate; formate; oxalate; malonate; and, acetate. As exemplary ligands for transition metal complexes, there may be mentioned: ethylenediaminetetraacetic acid (EDTA); diethylenetriaminepentaacetic acid (DTPA); hydroxyethylethylenediaminetriacetic acid (HEDTA); nitrilotriacetic acid (NTA); and, methylglycinediacetic acid (MGDA).

[0076] The conversion coating composition may optionally further contain at least one divalent metal cation (M^{2+}) selected from the group consisting of: Mg^{2+}; Ca^{2+}; Sr^{2+} and Ba^{2+}. The foregoing metal ions or mixtures thereof are most conveniently introduced into the composition as metal oxides, metal hydroxides and / or soluble and compatible metal salts, including but not limited to sulfate and halide salts. The use of nitrate and fluoride salts for this purpose is not preferred, however. For example, magnesium may be introduced into the aqueous conversion coating composition as one or more of: magnesium oxide, magnesium hydroxide; magnesium sulphate; and, magnesium chloride. A preference for magnesium oxide or magnesium hydroxide may be noted in this context.

Exemplary Formulation of the Conversion Coating Compositions

[0077] In an exemplary embodiment, which embodiment is not intended to be limiting of the present invention, there is provided an aqueous conversion coating composition having a pH of from 1 to 3, said composition comprising, based on the weight of the composition:

from 60 to 80 wt.% of water;
from 5 to 20 wt.% of 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP);
from 5 to 30 wt.% of phosphoric acid;
from 5 to 25 wt.% of fluoroacid, wherein said fluoroacid is selected the group consisting of fluorotitanic acid (H_2TiF_6), fluorozirconic acid (H_2ZrF_6) and mixtures thereof;
from 1 to 4 wt.% of tungstate salt, wherein said tungstate salt is selected from the group consisting of sodium orthotungstate (Na_2WO_4), sodium metatungstate ($Na_6H_2W_{12}O_{40}$), potassium orthotungstate (K_2WO_4), potassium metatungstate ($K_6H_2W_{12}O_{40}$) and mixtures thereof,

wherein the conversion coating composition is characterized in that it is substantially free of chromium (Cr) compounds.

Preparation of the Conversion Coating Compositions

[0078] The aqueous conversion coating compositions are formulated by simple mixing of the various components. If necessary, the composition may be prepared well in advance of its application. However, in an interesting alternative embodiment, a concentrated coating composition may first be obtained by mixing components with only a fraction of the water that would be present in the coating composition as applied: the concentrated coating composition may then be diluted with the remaining water shortly before its introduction into the passivation or coating bath. It is considered that such concentrated conversion coating compositions may be prepared and stored as either single-package concentrates - that can be converted by dilution with water only - or as multi-part concentrates, two or more of which must be combined and diluted to form a complete working composition according to the invention. Any dilution can be effected simply by the addition of water, in particular deionized and / or demineralized water, under mixing. The coating composition might equally be prepared within a rinse stream whereby one or more streams of the concentrate(s) is injected into a continuous stream of water.

[0079] Without specific intention to limit the amount of water included in the conversion coating compositions, it is preferred that said compositions contain from 25 to 80 wt.%, preferably from 40 to 80 wt.% and more preferably from 60 to 80 wt.%, based on the weight of the composition, of water. In an alternative but not mutually exclusive characterization, the conversion coating composition may be defined by a viscosity of from 0.005 to 1 Pa.s (50 cps to 1000 cps), as measured using a Brookfield viscometer at 25°C.

Methods and Applications

[0080] The aluminium and aluminium alloy substrate to be treated with the above described composition may be provided in various forms, including sheets, plates, cuboids, spheres, annuli, solid cylinders, tubes and wires: the provision of substrates in more complex, shaped forms - obtained by conventional techniques such as bending, blanking, casting, forging, rolling and welding - is of course not precluded. Moreover, the aluminium or aluminium alloy to be treated may, in some embodiments, be provided as a plating or a coating on a distinct base material, of which mention may be made of iron, nickel, copper, zinc and alloys thereof: base materials comprising or consisting of steel may be noted in particular.

[0081] In accordance with process aspects of the present invention, it is often advisable to remove foreign matter from the metal or alloy substrate by cleaning and degreasing the relevant surfaces. Such treatments are known in the art and can be performed in a single or multi-stage manner constituted by, for instance, the use of one or more of: a waterborne alkaline degreasing bath; a waterborne cleaning emulsion; a cleaning solvent, such as carbon tetrachloride or trichloroethylene; and, a water rinse, preferably of deionized or demineralized water. In those instances where a waterborne alkaline degreasing bath is used, any of the degreasing agent remaining on the surface should desirably be removed by rinsing the substrate surface with deionized or demineralized water.

[0082] Independently of or additional to the cleaning and degreasing treatments mentioned above, the surface(s) to be treated should preferably be deoxidized prior to being contacted with the acidic aqueous conversion composition. Such deoxidizing may include one or both of the mechanical or chemical removal of surface oxides from the surface to be coated. Desirably, at least 50%, for example a least 80% or at least 95% of the surface oxides are removed from the aluminium surface to be treated.

[0083] Irrespective of the cleaning or degreasing agent applied and the mode of deoxidation, there should not be a significant delay in time between the performance of these steps and the conversion treatment: corrosion resistance

may be deleteriously impacted where a significant delay occurs. Therefore, whilst an aluminium or aluminium alloy surface may be allowed to dry after a given pre-treatment stage - by for instance absorption or evaporation of the fluids concerned - the time between the final pre-treatment stage and the application of the conversion composition should desirably be less than 15 minutes, for instance less than 5 minutes or less than 2 minutes.

[0084] After said cleaning, degreasing and / or pre-treatment steps, the conversion coating composition is applied to the substrate. The conversion coating composition may be applied at ambient temperature or the temperature of the composition may be elevated prior to application to, for instance, a temperature in the range from 30°C to 90°C, for instance from 30°C to 70°C.

[0085] To produce a double-face plated sheet, it is conventional commercially that an operating bath as hereinbefore described is prepared and the conversion coating composition is applied to the substrate by, without limitation, immersion, flooding, air-atomized spraying, air-assisted spraying, airless spraying, highvolume low-pressure spraying and air-assisted airless spraying. The minimum contact time of the composition with the substrate is most broadly that time which is sufficient to form the desired passivate film thereon: that contact time can be as little as 1 second or as great as 15 minutes in that instance where the conversion treatment is being performed on metal that will be cold worked: however, dependent upon the pH and the concentration of the applied solution, a contact time of from 5 to 300 seconds, for example from 5 to 50 seconds, would be more typical.

[0086] In certain circumstances it will only be necessary to form a conversion coating on a single surface of the substrate. In the context of the present disclosure, the conversion coating might only be applied to that aluminium-plated surface of a steel substrate which is to form the outer side of a structure, the side which is exposed to environmental conditions: forming conversion coatings on both the inner and outer surfaces of such a plated steel material may be deleterious to the subsequent weldability of that material. Techniques for applying the conversion coating composition to only a singular surface include but are not limited to: painting; brushing; roll coating; wiping; air-atomized spraying; air-assisted spraying; airless spraying; highvolume low-pressure spraying; and, air-assisted airless spraying.

[0087] At the conclusion of the application step, the article is dried using, for instance, ambient air drying, circulating warm air, forced air drying or infrared heating. The surface temperature of the substrate is controlled during drying: the peak metal temperature (PMT) need not exceed 100°C and should, more particularly be in the range from 20 to 90°C, for example 50 to 75°C.

[0088] Subsequent to drying, it is not precluded that the article be subjected to: at least one water rinse to remove residual conversion coating composition therefrom; and / or, rinsing with a dilute silicate solution. The rinsed substrate may be dried after completion of the rinsing step(s) or, if applicable, after each rinse solution.

[0089] The above described treatment should desirably yield a protective passivate monolayer over the aluminium or aluminium alloy, which monolayer has a coating weight of from 10 to 100 mg/m^2, preferably from 10 to 50 mg/m^2. If the coating weight is less than 10 mg/m^2, the conversion coating may impart insufficient corrosion resistance. If the coating weight is larger than 100 mg/m^2, the adhesion of the coating to the surface will be insufficient, such that exfoliation of the coating may occur during further processing of the substrate.

[0090] The composition according to the present invention yields a coating that is bluish in color: the depth of the blue color is determined predominantly by the base substrate and by the immersion time of that substrate in the conversion coating composition. That said, the presence of coloration is considered to be beneficial *per se* as it permits a visual inspection of the coating quality to be made during and after its application. Such an inspection is not possible with zirconium coatings, for instance, which are largely transparent.

[0091] Alternatively or additionally, said aluminium or aluminium alloys passivated in accordance with the present invention exhibit corrosion protection for at least 200 hours before the observed onset of white rust corrosion (as defined by ASTM B-201) when treated with neutral salt spray (NSS, 5 wt.% NaCl, 95 wt.% H_2O) under steady state conditions in accordance with the procedure of ASTM B-117.

[0092] The present invention does not preclude supplementary conversion coatings being applied to the coating obtained in accordance with the present invention; indeed such supplementary coatings may further extend corrosion protection of the finished article. Inorganic coatings based on silicates and organic conversion coatings based on epoxy resins might be mentioned as non-limiting examples of supplemental conversion coatings: reference in this regard may be made to *inter alia* US Patent No. 5,743,971 (Inoue) and US Patent No. 5,855,695 (McMillen). These supplemental conversion coatings may be applied by any suitable means known in the art, such as by dipping, spraying, roll-coating, electro-coating or powder coating.

[0093] Various features and embodiments of the disclosure are described in the following examples, which are intended to be representative and not limiting.

EXAMPLES

[0094] The following commercial products are used in the Reference Compositions and the Composition according to the invention:

Codex 661: 1-Hydroxyethylidene-1,1-diphosphonic acid (aqueous, 60% concentration, CAS No. 2809-21-4) available from Excel Industries Limited.
Fluorotitanic Acid (FTA) Hexafluorotitanic acid (H_2TiF_6, aqueous, 50% concentration) available S.B. Chemicals.
Parco™ Cleaner 305: Liquid phosphate-free, alkaline spray cleaner, available from Henkel Technologies.
Ammonium bifluoride $[NH_4][HF_2]$, available from Sigma Aldrich.
Sodium orthotungstate: Na_2WO_4, available from Sigma Aldrich.

[0095] Aqueous conversion coating compositions were prepared by mixing the ingredients given in Table 1 herein below:

Table 1

Ingredient	**Inventive Composition (wt.% of composition)**	**Reference Composition 1 (wt.% of composition)**	**Reference Composition 2 (wt.% of composition)**
Water	48.0	63.0	62.5
Phosphoric acid (aq., 85% conc.)	20.0		10.0
Sulphuric acid		20.0	
Codex 661	10.0		15.0
FTA	20.0	15.0	10.0
Ammonium Bifluoride		2.0	
Magnesium oxide			2.5
Sodium orthotungstate	2.0		

[0096] Based on these tabulated aqueous compositions, the following tests were performed utilizing both the aqueous conversion coating compositions of the present invention and the reference compositions.

[0097] Standard Test Panel Preparation: Specimens of the aluminium substrate (Q-Panels AQ48 5005H24 aluminum mill finish) were mechanically cut into squares of 4cm x 4 cm dimensions. Each obtained panel was treated with an Parco™ Cleaner 305 (2.5% v/v) at 60°C for 10 seconds, rinsed with tap water at room temperature and then dried by squeegeeing. Each coating composition selected for evaluation was applied to one surface of the panels by roller coater. The resultant coated test panels were then baked to the peak metal temperature (PMT) given in Table 2 herein below. The obtained coating weight of the test panels was determined on a metals basis and is also given in Table 2.

[0098] Neutral salt spray (NSS): This test was carried out according to ASTM B117 with a 5% NaCl solution at 35°C (https://www.astm.org/Standards/B117). The coated panels were disposed in the spray chamber (ERICHSEN Model 606/400 L) at 15 - 30° from the vertical. The test panels were not allowed to contact other surfaces in the chamber and condensed or corrosion products on their surfaces were not permitted to cross-contaminate each other. Photographic recording of the test panels was performed each 24 hours. After a total exposure of 200 hours, test panels were rinsed in de-ionized water to remove salt deposits from their surface and then immediately dried. A final visual inspection of the coated panels was then undertaken.

[0099] Cross Hatch Test: This test provides a measure of the ability of a coating to adhere to a surface. Herein the Cross Hatch test was performed by: a) applying to the test panel an epoxy polyester powder coating (Apcoshield EXPY700G, Asian Paints) at a dry film thickness of 55-60 microns; b) forming a crosshatched area by making two perpendicular cuts on the powder coated test panel with a Gardener crosshatch tool having 10 knife edges spaced 1.5 mm apart; c) firmly applying #610 Scotch™ tape to the crosshatched area and removing the tape; and, d) examining the crosshatched area for paint not removed by the tape and report a number related to the percentage of powder coating remaining. The following 0-5 rating scale was used for recording the results of the Cross Hatch test: **0,** no pickoff; **1,** very slight pickoff from square edges; **2,** slight pickoff (1-2%); **3,** moderate pickoff (2-50%); **4,** severe pick off (>50%); and, **5,** very severe pickoff whereby crosshatching removes the coating.

[0100] The results of these tests are illustrated in Table 2 herein below.

Table 2

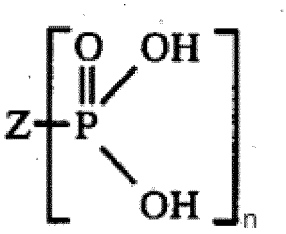
Test Condition	Composition 1	Reference Composition 1	Reference Composition 2
Composition pH	2.3	2.0	1.1
Composition Appearance	Pale yellow liquid	Colorless liquid	Colorless liquid
Peak Metal Temperature (°C)	55-60	55-60	55-60
Applied Coating Weight (mg/m^2, metals basis)	20-25	5-10	20-25
Initial Visual Inspection of Test Panel	Bluish tint	Transparent, colorless	Transparent colorless
Visual Inspection (NSS Test, 48 hours)	No rust	White black rust all over the surface	White black rust all over the surface
Visual Inspection (NSS Test, 200 hours)	No rust	White black rust all over the surface	White black rust all over the surface
Cross Hatch Test Rating	0	0	0

[0101] In view of the foregoing description and examples, it will be apparent to those skilled in the art that equivalent modifications thereof can be made without departing from the scope of the claims.

Claims

1. An aqueous conversion coating composition for the treatment of aluminium or aluminium alloys, said composition having a pH of less than 3 and comprising:

i) at least one water-soluble polyphosphonic acid or a water-soluble salt thereof, wherein said polyphosphonic acid has the general formula (I):



(I)

in which:

n is at least 2; and,
Z is a connecting organic moiety having an effective valency of n,
said polyphosphonic acid being **characterized in that** at least two phosphonic groups are separated by a C_1-C_2 alkylene bridge which may be optionally interrupted by one or more heretoatoms selected from N or O;

ii) at least one mineral acid;
iii) at least one water-soluble or water-dispersible fluoroacid or a salt thereof, wherein said fluoroacid is defined by the following general empirical formula (II):

$$H_pT_qF_rO_s \qquad (II)$$

wherein:

each of q and r represents an integer from 1 to 10;
each of p and s represents an integer from 0 to 10; and,
T represents an element selected from the group consisting of Ti, Zr, Hf, Si, Sn, Al, Ge, and B; and,

iv) at least one tungstate salt,

wherein said composition is **characterized in that** it is substantially free of chromium (Cr) compounds.

2. The composition according to claim 1 having a pH of from 1 to 3 and comprising, based on the weight of the composition:

from 25 to 80 wt.% of water;
from 5 to 25 wt.% of i) said at least one water-soluble polyphosphonic acid or a water-soluble salt thereof;
from 5 to 50 wt.% of ii) said at least one mineral acid;
from 5 to 35 wt.% of iii) said at least one water-soluble or water-dispersible fluoroacid or a salt thereof; and,
from 1 to 5 wt.% of iv) said at least one tungstate salt.

3. The composition according to claim 1 having a pH of from 1 to 3 and comprising, based on the weight of the composition:

from 40 to 80 wt.% of water;
from 5 to 20 wt.% of i) said at least one water-soluble polyphosphonic acid or a water-soluble salt thereof;
from 5 to 30 wt.% of ii) said at least one mineral acid;
from 5 to 25 wt.% of iii) said at least one water-soluble or water-dispersible fluoroacid or a salt thereof; and,
from 1 to 4 wt.% of iv) said at least one tungstate salt.

4. The composition according to any one of claims 1 to 3, wherein in general formula (I) n is an integer from 2 to 5.

5. The composition according to any one of claims 1 to 4, wherein said polyphosphonic acid is selected from the group consisting of: aminotris(methylene phosphonic acid) (ATMP); 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP); hexamethylene diamine tetra(methylene phosphonic acid) (HDTMP); diethylenetriamine penta(methylenephosphonic acid (DTPMP); and, mixtures thereof.

6. The composition according to claim 5, wherein said polyphosphonic acid comprises or consists of 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP).

7. The composition according to any one of claims 1 to 6, wherein said at least one mineral acid is selected from the group consisting of phosphoric acid, phosphonic acid, sulphurous acid and sulphuric acid.

8. The composition according to claim 7, wherein said mineral acid comprises or consists of phosphoric acid.

9. The composition according to any one of claims 1 to 8, wherein in formula (II):

T is selected from Ti or Zr;
p is 1 or 2;
q is 1;
r is 2, 3, 4, 5 or 6; and,
s is 0, 1, or 2.

10. The composition according to any one of claims 1 to 8, wherein said at least one fluoroacid is selected from the group consisting of: fluorotitanic acid (H_2TiF_6); fluorozirconic acid (H_2ZrF_6); fluorosilicic acid (H_2SiF_6); fluoroboric acid (HBF_4); fluorostannic acid (H_2SnF_6); fluorogermanic acid (H_2GeF_6); fluorohafnic acid (H_2HfF_6); and, fluoroaluminic acid (H_3AlF_6);

11. The composition according to claim 10, wherein said fluoroacid comprises or consists of fluorotitanic acid (H_2TiF_6).

12. The composition according to any one of claims 1 to 11, wherein iv) said at least one tungstate salt is selected from the group consisting of: lithium orthotungstate (Li_2WO_4); sodium orthotungstate (Na_2WO_4); potassium orthotungstate

(K_2WO_4); ammonium orthotungstate ($(NH_4)_2WO_4$); ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}$); potassium metatungstate ($K_6H_2W_{12}O_{40}$); and, sodium metatungstate ($Na_6H_2W_{12}O_{40}$).

13. The composition according to claim 12, wherein iv) said at least one tungstate salt is selected from the group consisting of: sodium orthotungstate (Na_2WO_4); sodium metatungstate ($Na_6H_2W_{12}O_{40}$); potassium orthotungstate (K_2WO_4); and, potassium metatungstate ($K_6H_2W_{12}O_{40}$).

14. The composition according to any one of claims 1 to 13 being substantially free of nitrate compounds.

15. A process for imparting a conversion coating to an aluminium or aluminium alloy substrate, said process comprising contacting at least one surface of the substrate with an aqueous composition as defined in any one of claims 1 to 14 at a temperature ranging from 20°C to 90°C for a period of time sufficient to form a coating thereon.

16. A coated substrate obtained by the process defined in claim 15.

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EUROPEAN SEARCH REPORT

Application Number
EP 23 15 0086

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	23 May 2023	Fodor, Anna

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