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(54) **NON CHROMATE COLORED CONVERSION COATING FOR ALUMINUM**

NICHTCHROMATIERTE GEFÄRBTE UMWANDLUNGSBESCHICHTUNG FÜR ALUMINIUM

REVÊTEMENT DE CONVERSION COLORÉ SANS CHROMATE POUR L'ALUMINIUM

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Description

[0001] The present invention relates to a process for the formation of colored conversion coatings on aluminum substrates using an acidic aqueous composition as defined in claim 1 on file. The invention further relates to an acidic aqueous composition as defined in claim 1 on file that can be used in such a process. The formation of chromium-free conversion layers on metal surfaces is covered by extensive prior art literature as cited, for example, in WO 94/28193. Such conversion layers are colorless and transparent so that the surface is bright in appearance. However, it is more desirable that the conversion coating as the result of the conversion treatment is immediately visually recognizable to the human eye. This allows to easily determine whether the process has been successfully accomplished resulting in a homogeneous product. Due to the lack of color, surface analysis, for example X-ray fluorescence, is required to analyze the result of the conversion treatment process. This laborious and more time-consuming approach is the reason that hexavalent chromium based products, which are known to be carcinogenic, are still used in the architectural aluminum market.

[0002] GB 2 097 024 A discloses a process for passivation of metal surfaces, particularly for treating zinc, cadmium and aluminium surfaces, for improving the corrosion resistance properties and to further enhance the appearance of such surfaces by imparting a yellow or a blue-bright coating thereto. Accordingly, there is a need for a process for the formation of colored conversion coatings on aluminum substrates using hexavalent chromium-free substances in order to avoid the usage and presence of carcinogenic substances in the process and the obtained product. The coatings thus produced should be readily and easily recognizable without the need for more laborious technical procedures.

The present invention provides such a coating process and is based on the inventors' finding that a colored conversion coating can be formed on aluminum substrates by bringing an aluminum substrate into contact with an acidic aqueous as defined in claim 1 on file comprising chromium(III), the elements Mo and/or W, a source of fluoride, and at least one oxidizing agent having a standard reduction potential in a range from +1,0 to +1,8 V (SHE).

The advantages of the thus produced coatings are that they allow to judge homogeneity of the product by the human eye. In addition, it has been found that the processes described herein provide for a corrosion resistant conversion with improved adhesion properties of organic layers which may be applied afterwards, for example in form of a paint, an adhesive layer or a protective layer, and the like. Additionally, compared to prior art compositions no expensive and time consuming disposal of hexavalent chromium substances is needed.

[0003] The present invention is thus directed to a process for the formation of colored conversion coatings on

aluminum substrates wherein an aluminum substrate is brought into contact with an acidic aqueous composition, comprising

- 5 a) 0.1 to 2 g/kg calculated with respect to the element Cr of at least one water-soluble compound as a source of chromium(III),
- b) 0.01 to 0.2 g/kg calculated with respect to the elements Mo and/or W of at least one water-soluble compound of the elements Mo and/or W,
- 10 c) at least one water-soluble compound as a source of fluoride,
- d) 0.01 to 1.0 g/kg calculated on a H_2O_2 equivalent basis of at least one oxidizing agent different from the components a) to c) having a standard reduction potential in a range from +1.0 to +1.8 V (SHE),

wherein the molar ratio of total fluoride of the at least one water-soluble compound according to component c) to the element Cr of the at least one water-soluble compound according to component a) is at least 3 : 1.

"At least one", as used herein, refers to 1 and more, for instance 1, 2, 3, 4, 5, 6, 7, 8, 9 or more. If this terms refers to compounds of the herein described compositions, this term does not refer to the amount of molecules, but rather to the type of compound. For example "at least one water-soluble compound as a source of chromium(III)" refers to one or more different types of water-soluble compounds as a source of chromium(III), for example different salts. Used in combination with a given amount, the given amount is intended to cover the total amount of the respective type of constituent as described above.

Generally, "about", as used herein, relates to $\pm 20\%$, preferably $\pm 10\%$ of the numerical value to which it refers. "About 200" thus relates to 200 ± 40 , preferably 200 ± 20 .

The amounts of all components of the herein described compositions are weight percentages relative to the total weight of the composition, unless explicitly otherwise indicated. Such amounts are intended to relate to the total amount of the type of component concerned in the composition, unless otherwise indicated. For example, an amount given with respect to the "at least one water-soluble compound as a source of chromium(III)" refers to the total amount of water-soluble compounds that can serve as a source of chromium(III) in the composition.

[0004] "Water-soluble", as used herein, refers to a solubility of at least 1 g of the respective compound in 1 kg of deionised water ($\kappa < 1 \mu S cm^{-1}$) at $20^\circ C$.

50 The compositions used in the process of this invention are substantially free of hexavalent chromium. "Substantially free", as used in this connection, means that the hexavalent chromium content is below 5 mol%, preferably below 1 mol%, of the total chromium content.

[0005] The acidic aqueous composition in a process according to the invention has a pH value between 0 and 7, preferably between 1 and 6, more preferably of 2,5 and 4, even more preferably of about 3. The pH value

may be adjusted by an acid, for example, an aqueous acid and/or by a buffer system well known to the skilled person. The acids can be, without limited to, HCl, HNO₃, H₂SO₄, and/or H₃PO₄, preferably H₂SO₄ or HNO₃. Furthermore, HNO₃ can be used as component d). A buffer system may be formed, for example, with a conjugated base of H₃PO₄ and/or ammonia. The pH in the context of this invention relates to the negative logarithm to base 10 of the activity of hydronium ions at a temperature of 25 °C.

[0006] In the described process according to the invention, the aluminum substrate is brought into contact with an acidic aqueous composition as defined in claim 1 on file with the contacting being achieved by any suitable method known in the art. Those can, for example, include spray-coating, dip-coating, spin-coating, printing and the like. The contacting step can be conducted manually or automatically. The aluminum substrate can be brought once or several times into contact with the acidic aqueous composition according to the present invention, for example, 1, 2, 3, 4, 5, 6, 7, 8, 9, and more times.

[0007] In a preferred embodiment of the present invention the aluminum substrate is brought into contact with the acidic aqueous composition in an immersion or spraying process, preferably in a spraying process. In a preferred embodiment the contact time is at least 10 seconds, but preferably not more than 600 seconds, more preferably not more than 200 seconds.

In a further preferred embodiment the temperature of the acidic aqueous composition in a process of this invention is at least 15 °C, but preferably not higher than 80 °C, more preferably not more than 70 °C.

[0008] The acidic aqueous composition according to the invention comprises the components described above being characterized herein further.

The at least one water-soluble compound as a source of chromium(III) may be any compound that is soluble in water according to the above definition. The preferred source for Cr(III) are salts of Cr(III), including, but not limited to, chromium(III)trifluoride (CrF₃), chromium(III)nitrate, chromium(III)acetate, chromium(III)gluconate and/or chromium(III)sulfate, preferably the source is chromium(III)trifluoride. Aside from those mentioned, other suitable salts may also be used, all of which are known to those skilled in the art. Examples for such salts are chromium(III)chloride hexahydrate, chromium(III)hydroxide, etc.

[0009] In the present invention, component a) of the acidic aqueous composition amounts to at least 100 ppm, more preferably more than 500 ppm, but preferably not more than 2 g/kg, more preferably not more than 1,5g/kg calculated with respect to the element Cr and relative to the aqueous acidic composition. The term "ppm" in the context of this invention relates to "parts per million of weight", so that 1 ppm equals to 0,0001 wt.-%.

The at least one water-soluble compound of the element Mo and/or W according to component b) of the acidic aqueous composition may be any compound that is sol-

uble in water according to the above definition. Examples of suitable compounds are known to those in the art and include, for example and without limitation, molybdates, phosphomolybdic acid, molybdenum chloride, tungstates, such as sodium tungstate, and the like. In a preferred embodiment, the water-soluble compound of the element Mo is a molybdate. Molybdates can be discrete or polymeric and have any suitable counterion.

[0010] In the present invention, component b) of the acidic aqueous composition amounts to at least 10 ppm, preferably to at least 20 ppm, but preferably to not more than 200 ppm, more preferably to not more than 100 ppm calculated with respect to the elements Mo and/or W and relative to the aqueous acidic composition.

The water-soluble compound as a source of fluoride according to component c) of the acidic aqueous composition may be selected from hydrofluoric acid, simple fluorides, such as sodium fluoride or chromium(III)fluoride, and also complex fluoro acids, such as fluorotitanic acid or fluoro-zirconic acid as well as their water-soluble salts. The at least one oxidizing agent, which is different from the components a) to c), has a standard reduction potential in a range from +1,0 to +1,8 V (SHE). This standard reduction potential refers to the commonly known standard hydrogen electrode (SHE), which is a redox electrode and the hydrogen's standard electrode potential is declared to be zero at all temperature to form a basis for comparison with all other electrode reactions. An "oxidizing agent" according to compound d) of this invention preferably does not encompass dissolved oxygen or water-soluble compounds of metal elements. Accordingly, "different from the components a) to c)" means that none of the compounds a) to c) can simultaneously be considered the oxidizing agent in the sense of the present invention, but that both have to be different species. In other words, this does also mean that the oxidizing agent is not a compound that falls within the definition of components a) to c), i.e. is no source for chromium(III), molybdenum, tungsten, or fluoride. The at least one oxidizing agent different from the components a) to c) may be, for example, HNO₃ or H₂O₂.

[0011] In the present invention, the amount of component d) of the acidic aqueous composition is in the range of 0.01 to 1.0 g/kg, more preferably of 0.05 to 0.5 g/kg calculated on a H₂O₂ equivalent basis.

In a further preferred embodiment component d) is selected from water-soluble peroxides and/or oxyacids of the elements nitrogen, sulfur or chlorine as well as their water-soluble salts, preferably from hydrogen peroxide.

[0012] In yet another preferred embodiment of invention, the amount of free fluoride within the acidic aqueous composition is in the range of 10 to 200 ppm and relative to the aqueous acidic composition. The free fluoride content in the acidic aqueous composition in a process of this invention can be determined directly in an acidic aqueous composition of this invention by making use of a calibrated fluoride-sensitive electrode at a temperature of 25 °C.

[0013] In a further preferred embodiment of the invention, the acidic aqueous composition comprises in total less than 50 ppm, more preferably less than 10 ppm of water-soluble compounds of the elements Zr and/or Ti relative to the total composition. These compounds tend to interfere with the formation of a colored conversion coating based on chromium(III) so that their presence is less preferred.

After contacting with the acidic aqueous composition described herein, the metal surfaces can be rinsed with water, for example with deionized water. Depending on the nature of the subsequent coating with organic polymers, the metal surfaces are optionally dried after rinsing with water. If the coating with organic polymers is carried out, for example, by immersing the metal surfaces in a water-based paint dispersion, there is no need for drying after rinsing. However, if the coating based on organic polymers is an adhesive or powder coating, for example, the metal surfaces are preferably dried before this step. The aluminum substrate may be provided in any shape, for example, as aluminum stripes, aluminum plates, or aluminum parts. The aluminum parts treated in accordance with the invention may be joined to other metal parts through the adhesive layer.

The aluminum substrate in a process of this invention may be provided in any shape, for example, as aluminum stripes, aluminum plates, or aluminum parts.

[0014] The aluminum substrate that is brought into contact with the acidic aqueous composition according to the first aspect of this invention, can be used without any pre-treatment or can be pre-treated, for example, with an alkaline cleaning solution or acidic descaling solution suitable for the inventive process. All of the pre-treatment methods and agents are well known to the skilled person. The pre-treating can be conducted manually or automatically. For example, the aluminum substrate can be briefly pickled in cold concentrated nitric acid or the surfaces may be alternatively rubbed down with a squeegee. Optionally, the substrate can be simply rinsed with water, for example with deionized water, and may additionally be descaled with an acidic solution. These treatments may be used separately or in combination. The solutions used for any pre-treatment may have a temperature suitable for the pre-treatment, preferably in a range from 10 to 70 °C, from 20 to 55 °C, or about 25 °C, depending on the solution and the desired effect of the solution. Furthermore, the aluminum substrates can be pre-treated for 0.5 to 20 minutes, preferably for 1 to 10 minutes, more preferably for about 3 minutes.

[0015] According to the invention an acidic aqueous composition is encompassed that comprises

- a) 0.1 to 2 g/kg calculated with respect to the element Cr of at least one water-soluble compound as a source of chromium(III),
- b) 0.01 to 0.2 g/kg calculated with respect to the elements Mo and/or W of at least one water-soluble

- compound of the elements Mo and/or W,
- c) at least one water-soluble compound as a source of fluoride,
- d) 0.01 to 1.0 g/kg calculated on a H₂O₂ equivalent basis of at least one oxidizing agent different from the components a) to c) having a standard reduction potential in a range from +1.0 to +1.8 V (SHE),

wherein the molar ratio of compounds according to component a) with respect to the element Cr to compounds according to component b) with respect to the elements Mo and/or W preferably ranges from 15 : 1 to 25 : 1, and wherein the molar ratio of total fluoride of the at least one water-soluble compound according to component c) to the element Cr of the at least one water-soluble compound according to component a) is at least 3 : 1. It is not necessary that the components a) to c) originate from different compounds. In that respect the water-soluble compound chromium(III)fluoride is both a component a) as well as a component c). On the other hand, a compound according to component d) by definition of this invention cannot be at the same time a compound of one of the components a) to c) and is thus different from these components.

In a preferred embodiment the molar ratio of total fluoride of the at least one water-soluble compounds according to component c) to the element Cr of the at least one water-soluble compounds according to component a) of the composition is not more than 10 : 1.

[0016] The total fluoride content in acidic aqueous compositions according to the second aspect of this invention can be determined as described in DIN 38 405-D-4-1 in a buffered sample volume (TISAB: "Total Ionic Strength Adjustment Buffer") taken from the acidic aqueous composition by making use of a calibrated fluoride-sensitive electrode at 25 °C sample volume temperature. All embodiments described herein with relation to the process of this invention are equally applicable to the compositions of this invention and vice versa. This especially means that all preferred embodiments disclosed herein in relation to the compositions used in the described processes apply similarly to the described compositions.

Examples

[0017] Within a process sequence as listed below aluminum panels (AA6060) have been treated in order to yield colored coatings. The coatings have been tested with respect to adhesion properties towards a polyester-based organic resin.

Cycle:

[0018]

1. Alkaline Cleaning (Ridoline G 34 A (3,5 %), 55 °C, 3 min)

2. Rinse
3. Acidic Etching (Grametal DX 255 A (3 %), 25 °C, 3 min)
4. Rinse
5. DI rinse
6. Conversion Coating Treatment (35 °C, 45 sec, Spraying Pressure: 1 atm)
7. DI rinse

[0019] According to the above-mentioned process sequence the aluminum panels had been treated while the conversion treatment was performed through making use of the following different conversion coating compositions.

Comparative Example CE1:

[0020]

- | | |
|--------|--|
| 34 ppm | Ti from H_2TiF_6 as source compound |
| 56 ppm | Maleic Acid - Methylvinylether Copolymer |
| 35 ppm | Polyvinylalcohol |

[0021] The pH value was 3.0 ± 0.1 .

Comparative Example CE2:

[0022] Conversion Coating Composition of Comparative Example CE2 comprising additionally 25 ppm Molybdenum from ammonium heptamolybdate as the source compound.

Example E1:

[0023]

- | | |
|-----------|--|
| 1,06 g/kg | Cr(III) from CrF_3 as source compound |
| 66 ppm | Zr from H_2ZrF_6 as source compound |
| 12 ppm | Mo from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ |
| 120 ppm | NH_4HF_2 |
| 50 ppm | H_2O_2 |

[0024] An amount of HNO_3 to adjust the pH value to 3.0.

Example E2:

[0025] Conversion Coating Composition of Example E1 comprising 25 ppm Molybdenum from ammonium heptamolybdate as the source compound.

Example E3:

[0026] Conversion Coating Composition of Example E1 comprising 50 ppm Molybdenum from ammonium heptamolybdate as the source compound.

Example E4:

[0027] Conversion Coating Composition of Example E1 comprising 100 ppm Molybdenum from ammonium heptamolybdate as the source compound.

[0028] All treated parts have been painted with a polyester powder coating (Corro-Coat PE-F series 2403, Jotun A/S, Norway) and cured for 20 min at 180-190°C.

[0029] Results in the Wet Adhesion Test are summarized in Table 1 and reveal that the examples according to the invention (E1-E4) adhere sufficiently to the aluminum panel and are superior to chromium-free compositions independent of the additional presence of molybdenum (CE1, CE2).

Table 1	
Example	Wet Adhesion Test*
CE1	0-0
CE2	3-4
E1	0-0
E2	0-1
E3	0-0
E4	2-1
* 2 hours exposure in deionized boiling water and 1 hour at 25°C at 40% air humidity; assessment of delamination at cross hatch cut according to DIN ISO 2409	

[0030] The visibility of Cr(III)-Mo conversion coating (E1-E4) starts with 12 mg/kg Mo and increases fast with further additions. 25-50 mg/kg Mo gives a very good color that appears to be ideal for real life application. Color intensity is similar to Ti-Mo technology (CE2).

Claims

1. Acidic aqueous composition comprising

- a) 0.1 to 2 g/kg calculated with respect to the element Cr of at least one water-soluble compound as a source of chromium(III),
- b) 0.01 to 0.2 g/kg calculated with respect to the elements Mo and/or W of at least one water-soluble compound of the elements Mo and/or W,
- c) at least one water-soluble compound as a source of fluoride,
- d) 0.01 to 1.0 g/kg calculated on a H_2O_2 equivalent basis of at least one oxidizing agent different from the components a) to c) having a standard reduction potential in a range from +1.0 to +1.8 V (SHE),

wherein the molar ratio of total fluoride of the at least one water-soluble compound according to component c) to the element Cr of the at least one water-soluble compound according to component a) is at least 3 : 1.

2. Composition according to claim 1 wherein the molar ratio of total fluoride of the at least one water-soluble compound according to component c) to the element Cr of the at least one water-soluble compound according to component a) is not more than 10 : 1.
3. Composition according to one or both of the claims 1 to 2 wherein the molar ratio of compounds according to component a) with respect to the element Cr to compounds according to component b) with respect to the elements Mo and/or W ranges from 15 : 1 to 25 : 1.
4. Composition according to one or more of the preceding claims wherein component a) amounts to at least 500 ppm, but preferably to not more than 1,5 g/kg calculated with respect to the element Cr.
5. Composition according to one or more of the preceding claims wherein component a) is selected from chromium(III)trifluoride, chromium(III)nitrate and/or chromium(III)sulfate, preferably from chromium(III)trifluoride.
6. Composition according to one or more of the preceding claims wherein component b) amounts to at least 20 ppm, but preferably to not more than 100 ppm calculated with respect to the elements Mo and/or W.
7. Composition according to one or more of the preceding claims wherein component b) is selected from water-soluble compounds of the element Mo, preferably from molybdates.
8. Composition according to one or more of the preceding claims wherein the amount of free fluoride is in the range of 10 to 200 ppm.
9. Composition according to one or more of the preceding claims wherein the amount of component d) is in the range of 0.05 to 0.5 g/kg calculated on a H₂O₂ equivalent basis.
10. Composition according to one or more of the preceding claims wherein component d) is selected from water-soluble peroxides and/or oxyacids of the elements nitrogen, sulfur or chlorine, preferably from hydrogen peroxide and/or nitrate ions, more preferably from hydrogen peroxide.
11. Process for the formation of colored conversion coat-

ings on aluminum substrates wherein an aluminum substrate is brought into contact with an acidic aqueous composition according to one or more of the preceding claims

12. Process according to claim 11 wherein the aluminum substrate is brought into contact with the acidic aqueous composition through an immersion or spraying process, preferably through an immersion process.
13. Process according to claim 12 wherein the contact time for the immersion process is at least 10 seconds, but preferably not more than 200 seconds.
14. Process according to claim 12 wherein the temperature of the acidic aqueous composition is at least 15 °C, but preferably not higher than 50 °C.

Patentansprüche

1. Saure wässrige Zusammensetzung, umfassend
 - a) 0,1 bis 2 g/kg, berechnet in Bezug auf das Element Cr, wenigstens einer wasserlöslichen Verbindung als Quelle von Chrom(III),
 - b) 0,01 bis 0,2 g/kg, berechnet in Bezug auf die Elemente Mo und/oder W, wenigstens einer wasserlöslichen Verbindung der Elemente Mo und/oder W,
 - c) wenigstens eine wasserlösliche Verbindung als Quelle von Fluorid,
 - d) 0,01 bis 1,0 g/kg, berechnet auf einer H₂O₂-Äquivalenzbasis, wenigstens eines Oxidationsmittels, das sich von den Komponenten a) bis c) unterscheidet und ein Standardreduktionspotenzial in einem Bereich von +1,0 bis +1,8 V (SHE) aufweist,

wobei das Molverhältnis der Gesamtmenge an Fluorid der wenigstens einen wasserlöslichen Verbindung gemäß Komponente c) zu dem Element Cr der wenigstens einen wasserlöslichen Verbindung gemäß Komponente a) wenigstens 3:1 beträgt.
2. Zusammensetzung nach Anspruch 1, wobei das Molverhältnis der Gesamtmenge an Fluorid der wenigstens einen wasserlöslichen Verbindung gemäß Komponente c) zu dem Element Cr der wenigstens einen wasserlöslichen Verbindung gemäß Komponente a) nicht mehr als 10:1 beträgt.
3. Zusammensetzung nach einem oder beiden der Ansprüche 1 bis 2, wobei das Molverhältnis von Verbindungen gemäß Komponente a) in Bezug auf das Element Cr zu Verbindungen gemäß Komponente b) in Bezug auf die Elemente Mo und/oder W zwischen 15:1 und 25:1 beträgt.

4. Zusammensetzung nach einem oder mehreren der vorangehenden Ansprüche, wobei Komponente a) wenigstens 500 ppm ausmacht, aber vorzugsweise nicht mehr als 1,5 g/kg, berechnet in Bezug auf das Element Cr. 5
5. Zusammensetzung nach einem oder mehreren der vorangehenden Ansprüche, wobei Komponente a) ausgewählt ist aus Chrom(III)trifluorid, Chrom(III)nitrat und/oder Chrom(III)sulfat, vorzugsweise aus Chrom(III)trifluorid. 10
6. Zusammensetzung nach einem oder mehreren der vorangehenden Ansprüche, wobei Komponente b) wenigstens 20 ppm ausmacht, aber vorzugsweise nicht mehr als 100 ppm, berechnet in Bezug auf die Elemente Mo und/oder W. 15
7. Zusammensetzung nach einem oder mehreren der vorangehenden Ansprüche, wobei Komponente b) ausgewählt ist aus wasserlöslichen Verbindungen des Elements Mo, vorzugsweise aus Molybdaten. 20
8. Zusammensetzung nach einem oder mehreren der vorangehenden Ansprüche, wobei die Menge an freiem Fluorid im Bereich von 10 bis 200 ppm liegt. 25
9. Zusammensetzung nach einem oder mehreren der vorangehenden Ansprüche, wobei die Menge der Komponente d) im Bereich von 0,05 bis 0,5 g/kg liegt, berechnet auf einer H₂O₂-Äquivalenzbasis. 30
10. Zusammensetzung nach einem oder mehreren der vorangehenden Ansprüche, wobei Komponente d) ausgewählt ist aus wasserlöslichen Peroxiden und/oder Oxysäuren der Elemente Stickstoff, Schwefel oder Chlor, vorzugsweise aus Wasserstoffperoxid und/oder Nitrationen, mehr bevorzugt aus Wasserstoffperoxid. 35
11. Verfahren zum Bilden von farbigen Konvertierungsbeschichtungen auf Aluminiumsubstraten, wobei ein Aluminiumsubstrat mit einer sauren wässrigen Zusammensetzung nach einem oder mehreren der vorangehenden Ansprüche in Kontakt gebracht wird. 40
12. Verfahren nach Anspruch 11, wobei das Aluminiumsubstrat mit der sauren wässrigen Zusammensetzung durch ein Immersions- oder Sprühverfahren, vorzugsweise durch ein Immersionsverfahren in Kontakt gebracht wird. 45
13. Verfahren nach Anspruch 12, wobei die Kontaktzeit für das Immersionsverfahren wenigstens 10 Sekunden beträgt, aber vorzugsweise nicht mehr als 200 Sekunden. 50
14. Verfahren nach Anspruch 12, wobei die Temperatur

der sauren wässrigen Zusammensetzung wenigstens 15 °C beträgt, aber vorzugsweise nicht höher als 50 °C.

Revendications

1. Composition acide aqueuse comprenant :

- a) de 0,1 à 2 g/kg, calculés par rapport à l'élément Cr, d'au moins un composé soluble dans l'eau en tant que source de chrome (III),
- b) de 0,01 à 0,2 g/kg, calculés par rapport aux éléments Mo et/ou W, d'au moins un composé soluble dans l'eau des éléments Mo et/ou W,
- c) au moins un composé soluble dans l'eau en tant que source de fluorure,
- d) de 0,01 à 1,0 g/kg, calculés par rapport à une base équivalente de H₂O₂, d'au moins un agent oxydant des composants a) à c) présentant un potentiel de réduction standard dans une plage allant de +1,0 à +1,8 V (SHE),

dans laquelle le rapport molaire de fluorure total de l'au moins un composé soluble dans l'eau selon le composant c) à l'élément Cr de l'au moins un composé soluble dans l'eau selon le composant a) est d'au moins 3:1.

2. Composition selon la revendication 1, dans laquelle le rapport molaire du fluorure total de l'au moins un composé soluble dans l'eau selon l'élément c) à l'élément Cr de l'au moins un composé soluble dans l'eau selon le composant a) n'est pas supérieur à 10:1.

3. Composition selon une ou plusieurs des revendications 1 à 2, dans laquelle le rapport molaire des composés selon le composant a) par rapport à l'élément Cr aux composés selon le composant b) par rapport aux éléments Mo et/ou W se situe dans une plage allant de 15:1 à 25:1.

4. Composition selon une ou plusieurs des revendications précédentes, dans laquelle le composant a) est présent en une quantité d'au moins 500 ppm, mais de préférence n'excédant pas 1,5 g/kg, calculée par rapport à l'élément Cr.

5. Composition selon une ou plusieurs des revendications précédentes, dans laquelle le composant a) est choisi parmi le trifluorure (III) de chrome, le nitrate (III) de chrome et/ou le sulfate (III) de chrome, de préférence comme le trifluorure (III) de chrome.

6. Composition selon une ou plusieurs des revendications précédentes, dans laquelle le composant b) est présent en une quantité d'au moins 20 ppm, mais de préférence n'excédant pas 100 ppm, calculée par

rapport aux éléments Mo et/ou W.

7. Composition selon une ou plusieurs des revendications précédentes, dans laquelle le composant b) est choisi parmi les composés solubles dans l'eau de l'élément Mo, de préférence parmi les molybdates. 5
8. Composition selon une ou plusieurs des revendications précédentes, dans laquelle la quantité de fluorure libre se situe dans la plage allant de 10 à 200 ppm. 10
9. Composition selon une ou plusieurs des revendications précédentes, dans laquelle la quantité de composant d) se situe dans la plage allant de 0,05 à 0,5 g/kg, calculée sur une base équivalente de H₂O₂. 15
10. Composition selon une ou plusieurs des revendications précédentes, dans laquelle le composant d) est choisi parmi les peroxydes solubles dans l'eau et/ou les oxyacides des éléments azote, soufre ou chlore, de préférence parmi le peroxyde d'hydrogène et/ou les ions nitrate, de manière plus préférée parmi le peroxyde d'hydrogène. 20
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11. Procédé de formation de revêtements de conversion colorés sur des substrats d'aluminium, dans lequel un substrat d'aluminium est amené en contact avec une composition acide aqueuse selon une ou plusieurs des revendications précédentes. 30
12. Procédé selon la revendication 11, dans lequel le substrat d'aluminium est amené en contact avec la composition acide aqueuse par un procédé d'immersion ou de pulvérisation, de préférence par un procédé d'immersion. 35
13. Procédé selon la revendication 12, dans lequel le temps de contact pour le procédé d'immersion est d'au moins 10 secondes, mais de préférence n'excède pas 200 secondes. 40
14. Procédé selon la revendication 12, dans lequel la température de la composition acide aqueuse est d'au moins 15 °C, mais de préférence n'excède pas 50 °C. 45

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REFERENCES CITED IN THE DESCRIPTION

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