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(54) **ACIDIC AQUEOUS COMPOSITION FOR PREPARING A CORROSION RESISTANT COATING ON A METAL SUBSTRATE, METHOD FOR TREATING THE METAL SUBSTRATE BY USING THE COMPOSITION**

(57) The invention relates to an acidic aqueous composition for preparing a corrosion resistant layer on substrates of aluminium, aluminium alloys, anodized aluminium, aluminized steel, zinc or zinc alloy coated steel, wherein the composition comprises:

trivalent chromium (Cr^{3+}):	0.04 – 6	g/l
zirconium (Zr^{4+}):	0.08 – 8	g/l
total fluoride (F^-):	0.1 - 9	g/l
stabilizing agent comprising a hydroxyl carboxylic acid or corresponding base(s) thereof		
(calculated as the acid)::	0.2 - 9	g/l

wherein

the molar ratio $\text{Zr}^{4+} : \text{Cr}^{3+}$ is in the range of 0.8 : 1 to 2.0 : 1;

the molar ratio $\text{Zr}^{4+} : \text{F}^-$ is in the range of 1: 5.5 to 1.0 : 2.0; and

pH is in the range of 3.0 - 5.0.

The invention also relates to an application method of this acidic aqueous composition.

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Description

[0001] The invention relates to an acidic aqueous composition for preparing a corrosion resistant coating on a metal substrate, a method of providing a corrosion resistant coating on a metal substrate, as well as a post-treatment composition, in particular for use in said method.

[0002] In the art mechanical and chemical treatment of metal surfaces for enhancing (bare) corrosion resistance, as well as for improving bonding to a subsequently applied coating such as an adhesive layer, paint layer, lacquer layer or other finishing layer and thereby enhancing the corrosion resistance of the thus coated final product is well known. E.g. mechanical treatment such as grit blasting has been used to improve adhesion, when chemical treatment steps were not practical to apply. Chemical treatment of metal surfaces of zinc (alloy) coated steel, mild steel, or aluminium and their alloys with aqueous chromate (chromium VI) solutions results in a so called "chromate conversion layer", which offers corrosion resistance and improved adhesion.

[0003] It has been recognized that these chromate based aqueous solutions suffer from the toxicity of the Cr^{6+} component thereof. Cr^{6+} is classified as carcinogenic and will be banned from most industrial applications involving high exposure risks for the operating staff. Disposal of the toxic treatment composition is also a problem, although to a lesser extent if the hexavalent chromium is converted into the comparatively innocuous trivalent chromium. However, such a conversion brings about additional costs and expenses.

[0004] Therefore, in the art there is a need for treatments that are substantially free of hexavalent chromium compounds, that offer corrosion resistance and bonding performance to the metal surfaces treated similar to those obtained by treating these metal surfaces with conventional solutions comprising hexavalent chromium. Proposals for satisfying this need, which are based on Cr(III) typically in combination with one or more other active components such as zirconium, are known.

[0005] From US 2011/0293841 A1 an aqueous solution for forming a protective coating on a metal surface is known that includes $\text{Cr}_2(\text{GF}_6)_3$, in which G is a Group IV-B element (Zr, Ti or Hf), in particular $\text{Cr}_2(\text{ZrF}_6)_3$ at least one polymer having a plurality of carboxylic acid groups such as polyacrylic acid and copolymers of methyl vinyl ether and maleic acid, and at least one polymer having a plurality of hydroxyl groups for example polyvinyl alcohols and homopolymers or copolymers of hydroxyethyl methacrylate, and/or at least one polymer having a plurality of both carboxylic acid and hydroxyl acid groups exemplified by free-radical copolymers of hydroxyl-ethyl methacrylate and methacrylic acid, wherein the composition contains less than 500 ppm of alkali metal ions and less than 200 ppm of halide ions relative to chromium. Application of a high purity $\text{Cr}_2(\text{ZrF}_6)_3$ solution, is said to improve the corrosion resistance of the metal substrate. The Zr : Cr molar ratio is typically determined by the stoichiometry of the compound, but due to the optional presence of other components the weight ratio Zr : Cr is typically in the range of 2.4 : 1 - 3.0 : 1, most typically 2.6:1 - 2.8:1. Any metal may be treated, with apparently good results being obtained on zinc, zinc alloy, aluminium and aluminium alloy surfaces. The addition of organo-functional silanes such as aminopropyl triethoxysilane may improve adhesion of subsequently applied coatings such as paints) to the treated surfaces, while maintaining good corrosion results. For a working bath the pH of a treatment solution comprising the above polymers is in a range from 2.5 - 4.0, more typically 2.8-3.2.

[0006] US 6375726 B1 has disclosed an acidic aqueous solution for the protection and surface treatment of aluminium, aluminium alloys and coated aluminium substrates against corrosion. The solution comprises at least one trivalent chromium salt such as trivalent chromium sulphate, at least one alkali metal hexafluorozirconate in combination with at least one water soluble or dispersible thickening agent and a water soluble surfactant. The corrosion resistant aluminium substrates of this invention have improved adhesion for overlaying coatings e.g. paints and a lower electrical resistance contact.

[0007] WO 2006/088519 A2 discloses an acidic aqueous solution for treating metal substrates, such as aluminium alloy or iron alloy or a metal substrate having a pre-existing metal coating for example anodized aluminium to improve the adhesion bonding and corrosion protection, which comprises water soluble trivalent chromium compounds, fluorozirconates, fluorometallic compounds, zinc compounds, thickeners, surfactants, and at least about 0.001 mole per litre of the acidic solution of at least one polyhydroxy and/or carboxylic compound as the stabilizing agent for the aqueous solution. The carboxylic compounds contain one or more carboxylic functional groups having the formula R-COO^- wherein R is hydrogen or a lower molecular weight organic radical or functional group, and can be used in the form of their acids or salts. The stabilizers are said to result in improved shelf-life and working stability of the solutions. According to this document after treating with the acid aqueous solution, application of a strong oxidizing solution can yield a film having additional corrosion resistance, which is presumed to be due to the formation of hexavalent chromium in the film derived from the trivalent chromium.

[0008] Furthermore an acidic, aqueous composition that contains a trivalent chromium compound, an organo-functional silane, and a compound of a group IV-B element, is known from US 2009/0280253 A1. The composition is said to protect metal surfaces, preferably aluminium and aluminium alloys, against corrosion and improves their paint adhesion. The trivalent chromium compound may comprise chromium fluoride and optionally others, such as chromium nitrate. The organo-functional silane is preferably an aminopropyltriethoxy silane, and the compound of a group IV-B element is

preferably fluoro-zirconic acid. The composition can either be dried-in-place or rinsed before a further coating layer is applied. The composition may also include at least one polymer having a plurality of both carboxylic functional groups, alone or with hydroxyl groups. The document also discloses a process using the aqueous composition either with or without the organo-functional silane along with a sealing step following the application of the aqueous composition; wherein the sealing step involves applying a sealing composition, including an organo-functional silane, to the metal surface.

[0009] From US 2015/0020925 A1 a process for surface treatment of a part made of aluminium, magnesium, or one of the alloys thereof, is known in order to protect the part from corrosion. The method comprises consecutively immersing the part in a first aqueous bath containing a corrosion-inhibiting metal salt such as trivalent chromium salt and an oxidizing compound such as K_2ZrF_6 , and a second aqueous bath containing an oxidizing compound like hydrogen peroxide and a corrosion-inhibiting rare-earth salt. The method can be carried out for the chemical conversion of aluminium or the alloys thereof, and of magnesium or the alloys thereof, on parts that have not been previously treated, or after anodizing the part to seal the anodic layer.

[0010] US 6648986 B1 teaches an acidic aqueous solution that contains a water soluble trivalent chromium compound, a water soluble fluoride compound, an alkaline pH adjustment reagent and provided with a solution stability additive for reducing precipitation of trivalent chromium over time. The solution stability additive comprises a complexing agent that is selected from the group consisting of organic acids (single coordination acids and bidentate chelating compounds) and amino acids. The concentration of the solution stability additive varies based on the complexing capability of the additive.

[0011] US 2010/0132843 A1 discloses a low sludge trivalent chromium based conversion coating bath that forms corrosion resistant coatings on aluminium and aluminium alloys by immersion in aqueous solutions containing trivalent chromium ions and fluorometallate ions followed by optional rinsing. Trivalent chromium coated aluminium also serves as an effective base for paint primers.

[0012] It is an object of the invention to provide a stable treatment solution based on Cr(III) for providing a substrate of aluminium, aluminium alloys, anodized aluminium, aluminized steel, zinc or zinc alloy coated steel with a layer, that protects the substrate against corrosion and/or offers adhesion for a subsequently applied (typically organic) coating such as paint, and/or for adhesive bonding system, or at least an alternative treatment solution.

[0013] Another object is to provide such a stable treatment solution that offers an enhanced layer formation.

[0014] A further object is to provide a method of applying a treatment composition to such a metal substrate in order to achieve corrosion resistance and/or adhesion.

[0015] Another object is to provide such a method that does not result in Cr^{6+} species in the deposited layer that are easily released from the treated product under severe conditions. Yet another object is to provide such a method that is easy to apply in maintenance and repair of aerostructural parts.

[0016] According to a first aspect the invention provides an acidic aqueous composition for preparing a corrosion resistant layer on substrates of aluminium, aluminium alloys, anodized aluminium, zinc or zinc alloy coated steel, aluminized steel, wherein the composition comprises:

trivalent chromium (Cr^{3+}):	0.04 - 6	g/l
zirconium (Zr^{4+}):	0.08 - 8	g/l
total fluoride (F^-):	0.1 - 9	g/l
stabilizing agent comprising a hydroxyl carboxylic acid or corresponding base(s) thereof (calculated as the acid):	0.2 - 9	g/l

wherein

the molar ratio $Zr^{4+} : Cr^{3+}$ is in the range of 0.8 : 1 to 2.0 : 1;
the molar ratio $Zr^{4+} : F^-$ is in the range of 1: 5.5 to 1.0 : 2.0; and
pH is in the range of 3.0 - 5.0.

[0017] It has been shown that the aqueous composition according to the invention when used as a bath is stable in time and does not form deposits and/or sludge in the bath. When applied to a surface of aluminium, aluminium alloys and anodized aluminium, zinc or zinc alloy coated steel, the surface, which is essentially free of Cr^{6+} , shows good corrosion resistance and if present, durable bonding to a subsequently applied paint system or adhesive bonding system.

[0018] The acidic aqueous composition according to the invention comprises as main active components trivalent chromium, tetravalent zirconium and fluoride in specific concentrations and ratios, as well as one or more hydroxyl carboxylic acids as stabilizing agent. Thereby a stable solution is provided with less fluoride with respect hexafluozirconic acid (H_2ZrF_6) or ((alkali) metal) salt thereof, wherein the ratio $Zr : F = 1 : 6$.

[0019] Trivalent chromium is present in an amount of 0.04-6 g/l, preferably 0.2-1.0 g/l for dipping and spraying applications. For touch-up, maintenance and repair applications using e.g. brushing and wiping a broader range of 0.5-5.0 g/L is advantageous. If the amount of chromium (III) is lower, then within industrially acceptable processing times, the rate of layer formation is low resulting in a layer having an insufficient thickness and thus inadequate protection and/or bonding.

[0020] The trivalent chromium can be derived from organic chromium salts, in particular citrate, glycolate, tartrate, and combinations thereof. Another attractive route for obtaining trivalent chromium is by reducing chromic acid (H_2CrO_4) with chemical agents that can be oxidized by chromic acid like methanol or hydrogen peroxide leaving no residual products in the starting solution after heating. Another attractive source for trivalent chromium and fluoride is using $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ as a starting material. This compound is hardly soluble in water, but accompanied by acidic components like HF, acidic hydroxyl carboxylic stabilizing agents and water soluble acidic polymers or combinations thereof, it is. HF is preferably used as it does not introduce extraneous anions other than those required.

[0021] Tetravalent zirconium is present in an amount of 0.08-8 g/l, preferably in the range of 0.2-2.0 g/l. Suitable starting materials comprise hexafluorozirconic acid and its ammonium salt, zirconium salts of lactate, carbonate, glycolate and citrate, ammonium zirconium carbonate and zirconium triethanol amine, and combinations thereof. The high zirconium content is believed to enhance co-precipitation of Cr and Zr as $\text{Cr}(\text{OH})_3$ and $\text{Zr}(\text{OH})_4$ and thereby layer formation.

[0022] F^- ions are present in the range of 0.1-9 g/l, preferably 0.2-2.0 g/l. The fluoride can be obtained from HF, alkali metal fluoride like sodium fluoride, ammonium bifluoride (ABF), chromium fluoride, hexafluoro zirconic acid and its ammonium salt, as well as combinations thereof. If hexafluoro zirconic acid is used as a starting material, at least one other zirconium component is present, otherwise the ratio of Zr : F is not within the required range. High fluoride contents compared to Cr and Zr results in excessive etching hindering layer formation. Without being bound to any theory it is believed that fluoride contents in the solution according to the invention will prevent over-etching during layer formation and might prevent accumulation of fluorides in the layer that could weaken the conversion layer during exposure in corrosive environment.

[0023] Low fluoride contents have the opposite effect and may reduce stability of the composition.

[0024] In addition to the concentration ranges the following molar ratio apply.

the molar ratio $\text{Zr}^{4+} : \text{Cr}^{3+}$ is in the range of 0.8 : 1 to 2.0 : 1; preferably 0.9:1 - 1.3 : 1, such as 1.04 : 1.0; and

the molar ratio $\text{Zr}^{4+} : \text{F}^-$ is in the range of 1: 5.5 to 1.0 : 2.0.

[0025] Then the molar ratio $\text{Cr}^{3+} : \text{F}^-$ is in the range of 1 : 11 to 1 : 1.6.

[0026] The acidic aqueous comprises a stabilizing agent being a hydroxy carboxylic acid or a corresponding base thereof in a concentration of 0.2-9 g/l, preferably in the range of 0.2- 5 g/l, more preferably 0.3 - 3 g/l (calculated as the acid). The stabilizing agent can be used as the acid or a water soluble salt thereof. Suitable hydroxyl carboxylic acids are lactic acid, citric acid, malic acid, tartaric acid, glycolic acid, gluconic acid and combinations thereof. The stabilizing agent may be introduced in the composition by the chromium or zirconium compound as well as shown above in the form of the zirconium and/or chromium (III) salt of the conjugated base of the hydroxy carboxylic acid, or as a similar part of the pH adjusting agents as discussed below. The stabilizing agent acts to stabilize the solution as a dipping bath having the composition according to the invention in time, which bath would otherwise at the given concentrations and ratios of its components deteriorate rapidly. It is assumed that the acid becomes part of the resulting layer comprising the hydroxides and oxides of chromium and zirconium. Higher contents of hydroxyl carboxylic acids results in coating layers that are sensitive to dissolving. Too low contents will cause instability and sludge forming of the composition during operation, typically a process bath for dipping, over time.. The composition according to the invention has a pH in the range of 3.0-5.0, preferably 3.4-4.4. If the pH is too low then the formation of the protective layer on the substrate is limited by the simultaneous attack of the formed layer by the acidic components. Thus the composition as a whole offers a balance between components and the amount thereof, their functional properties and processing possibilities. In order to set the acidity at the required level the composition may contain pH adjusting agents, typically bases, such as one or more alkali metal hydroxides like sodium hydroxide, potassium hydroxide and ammonia. As said before, the pH adjusting agent may be a source of the base of the hydroxyl carboxylic acid stabilizing agent. Examples include lactate, citrates of ammonium and/or sodium and the like. Advantageously the pH adjusting agent is present in amount of 0-1.0 g/l. The alkali metal cations do not - or to a negligible extent - affect the formation of the protective layer. When the pH rises to values above 5, the composition can easily become instable. At pH less than 3.0 it is hard to form substantial coating weight in view of corrosion resistance.

[0027] The composition may also comprise one or more water soluble surfactants for improving the wetting properties, advantageously in a concentration of 0-1.0 g/l, preferably 0.001-0.5 g/l. Surfactants that can be used in the composition according to the invention include acid stable low foaming anionic and non-ionic surfactants like alkaryl sulfonates and poly ethylene glycol fatty amines. The surfactant provides uniform wetting of the substrate. If the amount of surfactant is too high, it can cause excessive foaming in the process.

[0028] Other optional components of the composition according to the invention comprise water soluble polymers and

organo-functional silanes and/or their hydrolysed oligomers. The water soluble polymers include homopolymers and copolymers that preferably are based on the following monomers: acrylic acid, methacrylic acid, vinylalcohol, vinylether, maleic acid, monohydroxy acrylic ester, vinylphosphonic acid, vinylsulphonic acid, methyl vinylether, monohydroxy methacrylic ester and combinations thereof, up to 4.0 g/l, preferably 0.01-4.0 g/l, more preferably 0.1-1 g/l. These polymers improve wetting behaviour of the treatment composition, as well as adhesion of subsequently applied organic coatings. Too high concentrations will reduce wet adhesion of an organic coating. The concentration of the silanes or oligomers, if present, ranges up to 4.0 g/l. Advantageously the reactive functional group is at least one selected from a mercapto group, an amino group, a vinyl group, an epoxy group and a methacryloxy group, advantageously in an amount of 1 to 40 mg/l based on Si.

[0029] According to a second aspect the invention relates to a method of treating a substrate of aluminium, aluminium alloy, anodized aluminium, aluminized steel, zinc or zinc alloy coated steel for corrosion protection, adhesion of an organic coating or adhesive bonding system, which method comprises a step of applying the acidic aqueous solution according to the invention as explained above onto a substrate of aluminium, aluminium alloy, anodized aluminium, aluminized steel, zinc or zinc alloy coated steel.

[0030] Typically the metal surface to be treated with the composition according to the invention is pre-treated using known mechanical and/or chemical pre-treatment processes or combination thereof for obtaining a wettable surface, which typically requires the surface to be roughened and to be substantially free of rust, fat, oil and the like. Mechanical pre-treatment processes comprise grit blasting, shot peening, scuffing, scotch brite® and abrading. Chemical pre-treatment includes e.g. (acidic/alkaline/solvent) degreasing, de-oxidation, desmutting, pickling. Typically each chemical pre-treatment is followed by a rinsing step using tap water or demineralised water. Combinations of mechanical pre-treatment and chemical pre-treatment in any order is also possible. In case of aluminium or its alloys the surface may be anodized. Typically treatment according to the invention of bare aluminium will form a conversion layer. Treating anodized aluminium according to the invention will result in a sealing layer.

[0031] The way of applying the composition according to the invention to the metal surface is not limited. However, homogeneity and uniformity of the applied wet film on the substrate before drying will be advantageous. Suitable application methods include touch-up methods, spraying, dipping, wiping, brushing, roll coating and the like. Excess of treatment fluid on parts with intricate geometries can be removed with water rinsing, compressed air or wiping. After applying the acidic aqueous composition one or more rinsing steps with demi water are performed, preferably the last rinsing step with demi water having an electrical conductivity in the range of 5-200 microS, and a drying step of drying the thus rinsed substrate, in particular at a temperature in the range of 10-50 °C.

[0032] Advantageously the method according to the invention is performed with the composition having a temperature in the range of 10-80°C, preferably 15-50 °C. Typically the processing time ranges from 1-30 minutes, preferably from 3-15 minutes. Processing times of less than 3 minutes are practically not feasible on industrial scale in view of reproducible coating results. Processing times of more than 30 minutes may interfere with other operations on a continuous production line.

[0033] The coating weight, as measured by XRF after drying, is typically in the range of 5-200 mg Cr/m², such as 15-100 mg Cr/m². For a composition according to this invention coating weight can be controlled by adjusting concentration, pH, bath temperature and immersion time. Too high coating weights will give corrosion resistance, but may reduce adhesion properties and increase the surface electrical resistivity. Low electrical resistivity of the metal surface is important for certain applications as it prevents build-up of static electricity and will not influence welding properties.

[0034] It has appeared also that the method according to the invention is very suitable for maintenance and repair of damaged aluminium surfaces, like aerostructural parts, in particular where electrical resistivity of the resulting protective layer should be low, e.g. as detailed in MIL-DTL-5541F Class 3 coatings.

[0035] For certain alloys, in particular those copper containing aluminium alloys as used in the aerospace technical field such as 2024 and 7075, it has appeared advantageously to conduct a further treatment step. This further treatment step comprises post-treating the substrate that has been treated with the acidic aqueous composition, with a second acidic aqueous composition comprising an oxidizing agent and an acidifying component, which second composition has a pH in the range of 1-5, preferably 1-3. It has been shown that the risk of formation of Cr⁶⁺ in the formed protective layer is reduced by using the acidic second solution. Cr⁶⁺ was less than the detection limit (<0.03 µg/cm²) in the used second solution and in the thus obtained protective layer.

[0036] Advantageously the oxidizing component is a water soluble peroxide, preferably hydrogen peroxide. Hydrogen peroxide functions as a reductor with respect to Cr⁶⁺ in an acidic environment. Thus trivalent chromium will not be converted into hexavalent chromium. The concentration of the oxidizing component ranges typically from 10-100 g/l, preferably from 25-100 g/l.

[0037] The acidifying component is present in a concentration of 0.2-20 g/l, preferably 0.5-5.0 g/l. The acidifying component is advantageously a non-halogenated inorganic acid such as nitric acid, or a metal salt thereof excluding rare earth metals, preferably a salt of aluminium, zirconium and/or trivalent chromium, preferably the nitrate salt thereof. These acidic components should not dissolve the applied coating by the first composition nor etch aluminium. Nitric acid

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is a strong acid but has shown not to attack the coating from the first solution. Other strong acids like hydrogen chloride and sulphuric acid are too aggressive towards the first deposited layer. The second composition should be acidic enough to avoid formation of hexavalent chromium.

[0038] The temperature of the second composition is preferably in the range of 10-50 °C, more preferably at ambient temperature, like 20-30 °C. Such a low temperature is advantageous in order to avoid fast decomposition of peroxides.

[0039] Treating time is typically 1-30 minutes, preferably 3-15 minutes.

[0040] Suitable application methods for the second composition include spraying, dipping, wiping, brushing, roll coating and the like.

[0041] The invention is illustrated by the following Examples and Tests.

[0042] Composition 1 and 2 as indicated in Table 1 were prepared from commercially available compounds, as well as a Comparative Example without any hydroxy carboxylic acid. It appears that the composition of the Comparative Example is not stable

Table 1. Examples starting Compositions according to the invention and Comparative Example and their stability

	Composition 1 (wt. %)	Composition 2 (wt. %)	Comparative Example (wt.%)
Zirconium triethanolamine (13.8 wt. % Zr)	4		
Hexafluoro zirconium acid (19.8 wt. % Zr)	1.41		
Ammonium zirconium carbonate (14.8 wt.%Zr)		4.5	4.5
Chromium trifluoride *4 H ₂ O (28,7 wt.% Cr)	1.51	1,03	1.03
Hydrogen fluoride (20%)		0.9	0.9
Malic acid (99%)	0.9	0.7	
Remainder water			
Zr : Cr mol ratio	1.1 : 1	1.3 :1	1:3:1
Zr: F mol ratio	1 : 4.8	1 : 3.6	1:3.6
Stability (no suspension or gel formed)	> 240 days	> 240 days	< 1 day

[0043] From these starting Compositions first treatment solutions were prepared by dilution with demi water as indicated in Table 2. Table 3 lists compositions of the second treatment solutions.

Table 2 First treatment solutions (treatment 1 = TR1)

Examples TR1		[Zr] g/L	[Cr] g/L	[F] g/L	pH
C1	20 wt. % of Composition 1	1.66	0.87	1.65	3.9
C2	8 wt. % of Composition 2	0.53	0.24	0.4	3.9
C3	65 wt. % of Composition 2	4,31	1,95	3.2	3.6

Table 3 Second treatment solutions (treatment 2 =TR2)

Examples TR 2	composition	pH
P1	Al(NO ₃) ₃ *9H ₂ O, 4.33 g/l + H ₂ O ₂ (30%) 50 g/l	2.5
P2	Sulphuric Acid (1M) 5.33 g/L H ₂ O ₂ (30%) 50 g/l	2.1

(continued)

Examples TR 2	composition	pH
P3	HNO ₃ (1M) 34.63 g/L H ₂ O ₂ (30%) 50 g/l	1.9

[0044] Below Table 4 shows the various (optional) method steps and the conditions thereof, which are carried out according to the invention.

Table 4. General process conditions, preferred conditions and actual test values.

	Product	Concentration [wt.%]	Treatment time [min]	Temp. [°C]	pH
Alkaline degreasing	(Cleaner ABF)	3.0	3-7 (5)	50 -55 (53)	9 -10 (9.5)
Tap water rinsing					
Acidic deoxidation/ desmutting	(Adeox 11)	3.5	3-7 (5)	15 - 25 (20)	1- 3 (1)
Tap water rinsing					
Demi water rinsing					
First treatment solution	(C2)	5 - 20	2 - 20 [5 --15] (10)	10-- 80 [30 - 45] (40)	3-5 [3.4- 4.4] (3.9)
Demi water rinsing					
Forced hot air drying (optionally)				10-- 80 [40 --60]	
Second treatment solution	(P1)		0 --60 [3--7] (5)	5 -- 60 [15-- 30] (20)	1-5 [1-3] (2.5)
Demi water rinsing					
Forced hot air drying (optionally)			(10)	10-- 80 [40 -- 60] (60)	
[.] represent preferred ranges; (..) actual test value in below Example 2.					

Test 2

[0045] In this test set-up panels of aluminium alloys AA2024-T3 and AA2024-T81 were treated according to the steps in table 4 and actual values listed therein for C2. Neutral salt spray resistance according ASTM B117 was compared on the same alloy with the most common used hexavalent chrome conversion coating Alodine 1200S.

[0046] For the Alodine 1200S treated samples the aluminium substrate panels were subjected to the steps as summarized in below Table 5.

Table 5. Pre-treatment and treatment steps for Alodine 1200 treated samples

	Product	Immersion time [min]	Temperature [°C]
Alkaline Predegreasing	Turco 6849	10	60
Alkaline degreasing	Turco 4215	10	65
Tap water rinsing			
Acidic deoxidation/desmutting	Socosurf 1858	5	45
Tap water rinsing			

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(continued)

	Product	Immersion time [min]	Temperature [°C]
Demi water rinsing			
Conversion Coating	Alodine 1200S	2	RT
Demi water rinsing			

[0047] Per conversion coating, 5 panels were treated and subjected to the neutral salt spray test described in ASTM B117. After 168 hours of exposure the panels were evaluated according to MIL-DTL-81706. The test results are summarized in below Table 6.

Table 6. Test results

Al substrate		Pit count after 168 hrs NSS	
		Alodine 1200S	C2/P1
1	AA2024-T3	3	5
		0	3
		2	3
		1	3
		1	2
2	AA2024-T81	7	5+
		6	5+
		5	3
		6	3
		6	3

[0048] Corrosion resistance according to MIL-DTL-81706 requirements:

- (a) No more than 5 isolated spots or pits, none larger than 787 μm (0.031 in) diameter, per test specimen.
- (b) No more than 15 isolated spots or pits, none larger than 787 μm (0.031 in) in diameter, on the combined surface area of five test specimens, subjected to salt spray testing.

[0049] Table 7 shows data of the resulting layer weight of a conversion coating applied to AA2024 steel using 8 wt% solution of composition 2 (C2) under varying process time, using varying immersion (dipping) times, pH and T conditions.

[0050] The aluminium was pre-treated as listed in Table 4.

Table 7 Effect of varying process conditions on the resulting layer weight of the conversion coating on AA2024 (expressed in mg Cr/m²) using 8 wt.% of composition 2

		pH=4.2; T= 40°C		
Immersion t [min]		2	5	10
Coating weight {mg Cr/m ² }		12.5	18.8	24.1
		pH=4.2; t= 5 min.		
Temperature bath 1 [°]		30	35	40
Coating weight {mg Cr/m ² }		13.7	16.3	18.8

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(continued)

	t= 5 min; T=40°C		
pH bath 1	3.8	4	4.2
Coating weight {mg Cr/m ² }	11.6	13.3	18.8

Test 3

[0051] AA2024-T3 panels were treated with first treatment solution C1 under the same conditions as listed in Table 4 for C2 and various second treatment solutions.

[0052] Below Table 8 shows the corrosion test results of 2024 aluminium alloy, as well as the Cr⁶⁺ content present in conversion coating determined by boiling water extraction.

Table 8. Aluminium alloy 2024 treated by C1 at 40 °C during 10 minutes, followed by a post rinse using various second treatment solutions.

Second treatment solution	Corrosion rating Salt Spray Test ASTM B117 after 168 hours	Hexavalent chromium measured after boiling water extraction
None	>5 pits	
P1	2 pits	< 0.03 µg/cm ²
P2	2 pits	< 0.03 µg/cm ²
H ₂ O ₂ (30%) 50 g/l	1 pits	0.09 µg/cm ²
P3	3 pits	< 0.03 µg/cm ²

[0053] From the test data it appears that the corrosion resistance of an AA2024-T3 substrate that is treated with a (trivalent chromium) first treatment solution according to the invention and a (hydrogen peroxide) second treatment solution according to the invention is improved compared to that of the same Al substrate that is only treated with the first treatment solution. Moreover the test data indicate that less hexavalent chromium is formed on the substrate due to the acidic, but non-aggressive nature of the second treatment solution.

Test 4

[0054] Different Al alloys were treated according to actual conditions listed in Table 4. The below Table 9 lists the test results.

Table 9

	Coating weight [mg Cr/m ²]	contact resistance MIL-DTL-81706 B Class 3 conversion coating < 5 mΩ /in2 [mΩ / in2]	corrosion resistance MIL-DTL-5541F ASTM-B117 >168 hrs [hrs]
AA2024-T3	23	0.4	>168
AA2024-T81	15	0.5	>168
AA6061-T6	30	1.6	>3000
AA7075-T73	30	1.5	>168
AA5083-H111	41	2.3	>168

Test 5

[0055] The method and compositions according to the invention are also suitable for maintenance and repair purposes, such as maintenance of aeroplanes, using the so-called touch-up or brush (wipe) methods, wherein the respective Al parts are degreased and any oxide skin is removed mechanically. Thereafter the first and second treatment solutions according to the invention are applied using a double (vertical and horizontal) wipe technique with dust free cloth.

[0056] Various Al alloys were subjected to an acidic etching with Adeox 8 (100 g/L), rinsed with water and then treated with first treatment solution C3 and again rinsed. For AA2024-T3 thereafter second treatment solution P3 was applied, followed by a rinsing step with water. Electrical resistivity and general corrosion performance were tested as shown in below Table 10.

Table 10

Alloy	contact resistance MIL-DTL-81706 B Class 3 conversion coating		Corrosion resistance
	(asis < 5 mΩ /in ²) [mΩ/in ²]	168 hrs Salt Spray ASTM B117 (< 10 mΩ/in ²) [mΩ/in ²]	336 hrs Salt Spray ASTM B117 [pass/fail]
AA2014-T3	0.2	2.1	pass
AA5754	0.1	1.7	pass
AA6061-T6	0.1	0.5	pass
AA7075-T73	0.4	0.4	pass

[0057] Table 11 presents further corrosion results of various metal substrates when treated according to the invention with C2 and optionally P1..

Table 11. Overview corrosion test results various aluminium alloys treated with C2, optionally followed by post-rinse P1 at room temperature during 5 minutes.

Aluminium Alloy	C2	P1	Neutral Salt Spray < 5 pits ASTM B117
AA2024-T3	no	no	< 8hr
AA2024-T3	yes	no	>168 hr
AA2024-T3	yes	yes	>500 hr
AA5005	yes	no	>1000 hr
AA5754	yes	no	>1000 hr
AA6060	yes	no	>1000 hr
AA6061-T6	yes	no	>1500 hr
AA6061-T6	yes	yes	>3000 hr
AA6063	yes	no	>1000 hr

Test 6

[0058]

Table 12. Standard boric acid/sulphuric acid anodizing procedure on 2024 aluminium alloy 2024. Anodized coating thickness 5 μm . Anodized layer is treated /sealed with Composition 2 at 2 different concentrations ($T=40\text{ }^{\circ}\text{C}$, $t=10$ minutes) without post rinse.

Example	Immersion time [min]	Bath temperature [$^{\circ}\text{C}$]	Conc. Cr^{3+} [g/L]	Sealed according to this invention Measured Cr	Corrosion rating Salt Spray Test ASTM B117
1	-	-	-	-	completely corroded in 24 h
2	10	40	0,5	80 Cr mg/m^2	no pits after 168 h
3	10	40	0,25	40 Cr mg/m^2	3 pits after 168 h

Test 7

[0059]

Table 13. HDG (hot dip galvanized) Steel experiment

Substrate fresh hot dipped galvanized steel cooled down to $80\text{ }^{\circ}\text{C}$	Corrosion test Humidity 100% RH, $40\text{ }^{\circ}\text{C}$ Time to 5% white rust formation	Corrosion test: ASTM B117 Neutral salt spray test Time to 5% white rust formation
No treatment	< 12 hours	< 2 hours
10 wt.% Composition 2, Room Temperature, 10 minutes	500 hours	48 hours

Claims

1. An acidic aqueous composition for preparing a corrosion resistant layer on substrates of aluminium, aluminium alloys, anodized aluminium, zinc or zinc alloy coated steel, or aluminized steel, wherein the composition comprises:

trivalent chromium (Cr^{3+}):	0.04 - 6	g/l
zirconium (Zr^{4+}):	0.08 - 8	g/l
total fluoride (F^-):	0.1 - 9	g/l
stabilizing agent comprising a hydroxyl carboxylic acid or corresponding base(s) thereof (calculated as the acid):	0.2 - 9	g/l

wherein

the molar ratio $\text{Zr}^{4+} : \text{Cr}^{3+}$ is in the range of 0.8 : 1 to 2.0 : 1;
the molar ratio $\text{Zr}^{4+} : \text{F}^-$ is in the range of 1: 5.5 to 1.0 : 2.0; and
pH is in the range of 3.0 - 5.0.

2. The composition according to claim 1, wherein the concentration of trivalent chromium (Cr^{3+}) is in the range of 0.2-1.0 g/L or in the range of 0.5-5.0 g/L.
3. The composition according to claim 1 or 2, wherein the concentration of zirconium (Zr^{4+}) is in the range of 0.2-2.0 g/L.
4. The composition according to any one of the preceding claims, wherein the concentration of fluoride ions (F^-) is in the range of 0.2-2.0 g/L.
5. The composition according to any one of the preceding claims, wherein the concentration of stabilizing agent comprising a hydroxyl carboxylic acid or corresponding base(s) thereof (calculated as the acid) is in the range of 0.2-5 g/L, preferably 0.3-3 g/L.

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6. The composition according to any one of the preceding claims, wherein the pH is in the range of 3.4-4.4..
7. The composition according to any one of the preceding claims comprising one or more of water soluble surfactants in a concentration of 0-1.0 g/L, preferably 0.001-0.5 g/L, pH adjusting agents in a concentration of 0-1.0 g/L, water soluble polymers, organo functional silanes or oligomers in a concentration of up to 4.0 g/L.
8. A method of treating a substrate of aluminium, aluminium alloy, anodized aluminium, aluminized steel, zinc or zinc alloy coated steel for corrosion protection, adhesion of a coating or adhesive bonding system, which method comprises a step of applying the acidic aqueous solution according to any one of the preceding claims 1-7 to a substrate of aluminium, aluminium alloy, anodized aluminium, aluminized steel, zinc or zinc alloy coated steel.
9. The method according to claim 8, wherein the composition has a temperature in the range of 10-80 °C, preferably 15-50 °C.
10. The method according to claim 8 or 9, wherein the treatment time is 1-30 minutes, preferably 3-15 minutes.
11. The method according to any one of the preceding claims 8-10, further comprising one or more steps of rinsing the treated substrate with demineralized water, wherein preferably the last rinsing step is carried out using demineralized water having a conductivity in the range of 5-200 microS, and more preferably a step of drying the rinsed substrate, in particular at a temperature of 10-50 °C.
12. The method according to any one of the preceding claims 8-11, wherein the coating weight is in the range of 5-200 mg chromium/m², as measured by XRF after drying.
13. The method according to any one of the preceding claims 8-12, further comprising a step of after-treating the substrate that has been treated with the acidic aqueous composition according to any one of claims 1-7 with a second acidic aqueous composition comprising an oxidizing agent and an acidifying component and having a pH in the range of 1-5, preferably 1-3.
14. The method according to claim 13, wherein the concentration of the oxidizing agent is in the range of 5-100 g/L, preferably 8-50 g/L, and/or wherein the oxidizing agent is a water soluble peroxide, preferably hydrogen peroxide,
15. The method according to any one of the preceding claims 13-14, wherein the concentration of the acidifying component is in the range of 0.2-20.0 g/L, preferably 0.5-5.0 g/L, and/or wherein the acidic component is a salt of aluminium, zirconium or trivalent chromium, preferably a nitrate salt thereof.



EUROPEAN SEARCH REPORT

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