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(71) Applicant: **AD Productions B.V.**
4794 SN Heijningen (NL)

(72) Inventors:
- **van der NET, Richard Johannes**
  3329 AG DORDRECHT (NL)
- **LANGELAAR, Robin Arthur**
  4611 GC BERGEN OP ZOOM (NL)
- **van MEER, Roland Lambertus Maria**
  4791 HK KLUNDERT (NL)

(74) Representative: **EP&C**
P.O. Box 3241
2280 GE Rijswijk (NL)

(54) METHOD OF TREATING METAL SURFACES WITH AN AQUEOUS COMPOSITION AND AQUEOUS COMPOSITION

(57) The invention relates to a method of treating a metal surface of iron or iron alloy using an aqueous composition for imparting corrosion resistance and bonding properties, as well as to the aqueous composition. The aqueous composition consists of:

trivalent chromium (Cr^{3+}):	1.16-7.0	g/l
total fluoride (F^-):	1.3-7.7	g/l
organic corrosion inhibitor:	up to 2.0	g/l
water soluble polymers:	0-4.0	g/l
water soluble surfactant	0-1.0	g/l
organofunctional silane and/or oligomer	0-4.0	g/l
pH adjusting agent	0-1.0	g/l
fluoride adjusting agent	0-1.0	g/l

wherein the molar ratio of $Cr^{3+}$to F^- ranges from 0.25-0.4, and wherein the pH ranges from 2.0-4.4.

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Description

[0001] The invention relates to a method of treating metal surfaces with an aqueous composition and to an aqueous composition for treatment of metal surfaces.

[0002] Mechanical and chemical treatment of metal surfaces for enhancing corrosion resistance and/or improving bonding to a subsequently applied coating such as an adhesive layer, paint layer, lacquer layer or other finishing layer is well known in the art. E.g. mechanical treatment for example grid blasting has been used to remove scale and/or oxides from the metal surface and to improve adhesion, when chemical treatment steps were not practical to apply. Only waterborne cleaning of metal parts made of especially iron and iron alloys without any suitable chemical treatment will result in flash rusting (also known as "rapid corrosion"), if the parts are not painted within a few hours. Degreasing of oiled surfaces using a suitable solvent like thinner or heptane does not give rise to flash rusting. However, solvent degreasing offers considerable health and safety risks for personnel and the environment. 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, and avoids the occurrence of flash rusting before painting.

[0003] It is also 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 with high exposure risks for the co-workers. Disposal of the toxic treatment composition is also a problem, although to a lesser extent if it is converted into the comparatively innocuous trivalent chromium. However, such a conversion brings about additional costs and expenses.

[0004] Also phosphate coatings have been used to improve adhesion of coatings, such as paint, and corrosion resistance of steel. Some major disadvantages of phosphate coatings are necessity of several rinsing steps, sludge disposal and power consumption. Additionally these coatings are often sealed with a hexavalent chromium solution for optimum adhesion and corrosion. Therefore these phosphate coatings suffer from several environmental, health and safety drawbacks.

[0005] Today the use of chromate-free (paint) primers has become more common. It has appeared that mechanical and chemical pre-treatments of metals become more important to guaranty corrosion protection performance of metal paint systems.

[0006] Ongoing legislation is also developed and comes gradually into force in order to reduce and ultimately abandon hexavalent chromium based metal treatment compositions.

[0007] 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.

[0008] Various proposals to satisfy this need have been disclosed in the patent literature. E.g. WO 2006/088518 has disclosed a process for preparing zirconium-chromium conversion coatings on iron and iron alloys to improve the corrosion resistance and adhesive bonding strength. This known method comprises treating iron and iron alloys with an acidic aqueous solution having a pH ranging from about 2.5 to 5.5, preferably 3.7-4.0 for steel surfaces. The acidic aqueous solution comprises, per litre of solution, from about 0.01 to 22 grams of a trivalent chromium compound, about 0.01 to 12 grams of a hexafluorozirconate, about 0.0 to 12 grams of at least one fluorocompound selected from the group consisting of tetrafluoroborate, hexafluorosilicate and mixtures thereof, from about 0.0 to 10 grams of at least one divalent zinc compound, from 0.0 to about 10 grams of at least one water soluble thickener and from 0.0 to about 10 grams of at least one water soluble surfactant. Above known treatment contains at least zirconium and the preferred soluble trivalent chromium species is containing a sulphate anion. These extraneous cations and anions will affect the formation to insoluble species negatively. Therefore the remaining unreacted solution should be rinsed from the substrate with tap or demineralised water resulting in an additional waste stream that requires disposal or other processing.

[0009] WO 2006/088519 A1 discloses a similar treatment, wherein the solution also comprises a stabilizing compound selected from polyhydroxy and carboxylic compounds. In practice, these preparations are used at low concentrations of the effective species to avoid over-etching and flash rust during drying. However, low concentrations result in less dense protective layers on the metal surface and therefore might affect the protective and/or bonding performance.

[0010] From EP 111897 A1 a no-rinse process for treating metal surfaces is known, particularly for the subsequent application of organic coating compositions, in which the metal surface is wetted with an aqueous bath solution having a pH in the range of 2-3 and containing 0.5-10 g/L of chromium-(III) ions, 0.55-11 g/L of fluoride ions, 0.6-12.5 g/L of phosphate and 0.15-5.0 g/L of an organic film-forming agent which is soluble or homogeneously dispersible in water, like a water-soluble acrylic polymer.

[0011] An object is to provide a method of protecting an organic coated surface of iron or iron alloy against corrosion and/or improving durable adhesion properties of such an organic coating or an adhesive using a metal surface treatment solution.

[0012] Another object of the invention is the provision of an alternative metal treatment method and solution based

on trivalent chromium for protection of an organic coated surface of iron or iron alloy against corrosion and/or for improvement of the adhesion properties of such an organic coating or an adhesive using a metal surface treatment solution..

[0013] Yet another object is to provide a dry-in-place metal treatment method and solution requiring no rinse step after application.

[0014] Yet another object is to provide a dry-in-place metal treatment solution for use at room temperature on iron and iron alloys without flash rusting.

[0015] Still another object is to provide a metal treatment method and solution for application to an already phosphated surface of iron and iron alloy replacing a conventional chromate seal on such surface.

[0016] Accordingly, in a first aspect the invention provides a method of treating a metal surface of iron or iron alloy for providing corrosion protection, adhesion of coating and/or adhesive, which method comprises the application of an aqueous composition onto the metal surface of iron or iron alloy,
which composition consists of:

trivalent chromium (Cr^{3+}):	1.16-7.0	g/l
total fluoride (F^-):	1.3-7.7	g/l
organic corrosion inhibitor:	up to 2.0	g/l
water soluble polymers:	0-4.0	g/l
water soluble surfactant	0-1.0	g/l
organo functional silane and/or oligomer	0-4.0	g/l
pH adjusting agent	0-1.0	g/l
fluoride adjusting agent	0-1.0	g/l

wherein the molar ratio of Cr^{3+} to F^- ranges from 0.25-0.4, and wherein the pH ranges from 2.0-4.4.

[0017] In a second aspect the invention provides an aqueous composition as defined above for treating a metal surface of iron or iron alloy.

[0018] Below the invention is explained first of all in terms of composition and components thereof. The aqueous composition according to the invention is free of hexavalent chromium and contains as main constituents trivalent chromium ions and fluoride ions in a molar ratio of $Cr^{3+}$to F^- ranging from 0.25-0.4. Surprisingly it has been found that a solution having a relatively simple composition regarding its components without the need of specific more complex (fluorometalate) compounds as a source of fluoride ions offers good results regarding corrosion resistance and adhesion. These fluorometalate compounds as used in the prior art will introduce extraneous polyvalent metal ions and these are believed not to play a significant role regarding corrosion resistance and adhesion and could complicate the preparation of the composition regarding desired ratios of components. Contrary thereto the composition according to the invention can be easily prepared. Inorganic anions other than fluorides like phosphates are advantageously absent in the composition according to the invention. These other inorganic anions increase the solubility of the resulting conversion layer and affect its performance. Also stability and maintenance of the treatment bath might become more complicated. Metal surfaces that can be suitably treated with the composition according to the invention include iron and iron alloys such as cold rolled steel, mild steel and carbon steels. The metal surface may have a conventional phosphate conversion coating applied to it, before it is exposed to the composition according to the invention. The composition can be easily applied, even in repair and maintenance conditions such as outdoor pipeline field applications, ship-building, road work, offshore, industrial equipment and other (non-mobile) steel structures. Typically the composition can be applied directly to the metal surface, after conventional mechanical and/or chemical pre-treatment, such as grit blasting, sanding and scuffing and degreasing/pickling respectively. Rinsing after application of the composition is not necessary. The treatment solution can be dried in air under prevailing conditions and does not require any special measures or apparatuses. However the treated metal substrate should be dry before subsequent painting or adhesive bonding processes are carried out. In order to reduce process time forced drying methods can be used for example oven-drying, infra-red drying and forced-air drying. After the composition has been applied and sufficiently dried, the thus treated surface of iron or iron alloy can be coated with an organic paint, optionally including the pre-application of a paint primer, and/or with an adhesive bonding system.

[0019] The layer formed from the composition enhances the adhesion of the subsequently applied coating such as a paint layer system or adhesive bonding system. The enhanced adhesion offers good corrosion resistance when the thus coated metal surface is exposed to corrosive conditions. Furthermore, it has appeared that the layer formed may allow to reduce the layer thickness of a conventional paint primer or to waive the conventional primer at all .. Trivalent chromium is present in amount of 1.16-7.0 g/l. A preferred range is 3.0-6.0 g/l. Total fluoride is in the range of 1.3-7.7 g/l. The molar ratio of Cr^{3+} to F^- is 0.25-4.0, preferably 0.30-0.36, more preferably 0.32-0.34, such as 1:3. It has been found that the stoichiometric ratio of CrF_3 or slightly above offer good results regarding corrosion resistance and/or bonding charac-

teristics.

[0020] The trivalent chromium can be obtained 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 is using $CrF_3.4H_2O$ as a starting material. This compound is hardly soluble in water, but accompanied by acidic components like HF and acidic homopolymers and copolymers it is. HF is preferably used as it does not introduce extraneous anions.

[0021] The pH ranges from 2.0-4.4, preferably 2.7-3.8, in particular 2.7-3.4. In order to set the acidity at the required level the composition may contain pH adjusting agents, such as alkali metal hydroxide like sodium hydroxide, potassium hydroxide, and ammonia, in an amount of 0-1.0 g/l. It is believed that alkali metal ions do not - or to a substantially lesser extent-contribute to the formation of the protective layer and thus its protection and/or bonding properties.

[0022] As said, the molar ratio of fluoride to trivalent chromium is preferably equal to or slightly above the stoichiometric ratio of CrF_3. Adjustment may be carried out by incorporating of fluoride adjusting agents that offer an additional source of fluoride anions. If present, these fluoride adjusting agents are present in an amount up to 1.0 g/l. Preferred examples include fluoric acid, fluorides of alkali metals and ammonium, in particular sodium fluoride and ammonium bi fluoride.

[0023] The composition according to the invention contains an organic corrosion inhibitor in amount up to 2.0 g/l, preferably 0.0001-2.0, more preferably 0.1-1.0 g/l. Thus the organic corrosion inhibitor is a required component of the composition according to the invention. The organic corrosion inhibitor can act as a flash corrosion inhibitor, which inhibits so called "flash rusting" during drying of the applied treatment composition on iron and iron alloys surfaces. In addition the organic corrosion inhibitor is thought to contribute to the final corrosion resistance after application of a coating like paint. The organic corrosion inhibitor should be slightly soluble in water or miscible therewith. Examples include: N,N- dimethyl propylene urea, tolytriazole, zinc phthalate, imidazolinemaleate, caprylic acid, phtalic acid, phosphonic acid alkylesters, n-butyric acid, benzotriazole, tolytriazole, phthalate divalent salts, nitrobenzoate, 1-octanol, tannic acid, nitro maleate divalent salts, 2-mercaptobenzimidazole, propargyl alcohol, propargyl alcohol ethoxylates, iso nitro phtalate zinc salt, 2-butyn 1,4 diol, 2-butyn 1,4 diol alkoxylates, alkanolamine salt of a nitrogenous organic acids, quaternary amines and combinations thereof.

[0024] Concentration and the nature of the organic corrosion inhibitor or a mixture of corrosion inhibitors should be chosen in a way that it will not block the trivalent chromium deposition on the metal during treatment..

[0025] In addition to the above components the composition may comprise additional components from a selected group of optional compounds. These optional compounds include water soluble homopolymers and copolymers that preferably are based on the following monomers: acrylic acid, methacrylic acid, vinylalcohol, vinylether, maleic acid, vinylphosphonic acid, vinylsulphonic acid, methyl vinylether 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. Another optional compound is a water soluble surfactant, which may be present in an amount up to 1.0 g/l. A preferred concentration range is 0.001-0.5 g/l, while a more preferred concentration ranges from 0.01-0.1 g/l. Surfactant 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 and efficient removal of oil and dirt. If the amount of surfactant is too high, it can cause excessive foaming in the process.

[0026] Yet another component that may be present, is an organo functional silane and/or a hydrolysed oligomer thereof. If present, the concentration ranges up to 4.0 g/l. 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.

[0027] The method of treating a metal surface of iron or iron alloy for providing corrosion resistance and adhesion of a coating and or adhesive, comprises a step of applying the aqueous composition according to the invention and outlined hereinabove to the metal surface. Typically the metal surface to be treated with the composition according to the invention is pre-treated using known mechanical or chemical pre-treatment processes or acombination thereof for obtaining a better wettable surface, which typically requires the surface to be roughened and to be substantially free of rust, scale and oxides, fat, oil and the like. Mechanical pre-treatment processes comprise dry grit blasting, sanding, scuffing and abrading. Chemical pre-treatment include (acidic/alkaline/solvent) degreasing and pickling. Typically a 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.

[0028] It has surprisingly been found that the composition according to the invention can also replace degreasing using a solvent on oiled surfaces of iron or iron alloy, that are free of scale and oxides. Upon application of the composition according to the invention, in particular a present composition containing a surfactant, on such surfaces removal of oil, fat and dirt and building of the conversion layer occur simultaneously, rendering a preceding solvent degreasing step superfluous. Thus in an embodiment of the method according to the invention involves contacting an oiled, but scale and oxide free surface of iron or iron alloy with the present composition.

[0029] The composition according to the invention allows also to replace a conventional chromate seal on an already phosphated surface of iron and iron alloy.

[0030] 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 spraying, dipping, wiping, brushing, roll coating and the like. Excess of treatment fluid on parts with intricate geometries can be removed with compressed air before drying. After application it is not necessary to perform a rinsing step to remove unreactive and/or unreacted species from the formed layer. Instead thereof the metal surface to which the composition according to the invention is applied can be allowed to dry immediately, e.g. in air optionally at elevated temperature like an oven having conditioned air.

[0031] Advantageously the coating weight (after drying measured by XRF (X ray fluorescence)) ranges from 20 to 200 mg chromium/m^2. Higher coating weights will reduce adhesion properties of subsequently applied organic coating layers. At lower coating weights no beneficial effect in corrosion protection has been measured.

[0032] A subsequently applied paint system and/or adhesive bonding system can be applied using conventional methods and equipment, such as spraying, brushing and roll coating.

[0033] The various features of the treatment composition as discussed above are equally applicable to the method according to the invention.

[0034] The invention is illustrated by the following examples according to the invention and comparative examples.

[0035] The trivalent chromium compound "Cr(III) Fluoride" as indicated in the below Tables was obtained by reducing a chromic acid solution in a stoichiometric ratio chromium to fluoride 1 to 3.The fluoride source was an aqueous solution of hydrogen fluoride. Methanol in water was used as a reducing agent. After 4 hours of reduction at 80 °C no hexavalent chromium could be detected by using a s-diphenylcarbazide test method (detection limit for Cr(VI) is smaller than 0.03 ppm). Methanol and oxidation products of methanol like formalin and formic acid could not be detected by TOC (total organic carbon) measurements.

[0036] Aqueous metal surface treatment liquids having a composition as indicated in Table 1 were prepared and applied to metal surfaces as indicated in Tables 2-4..

[0037] The thus pre-treated, treated and organic coated surfaces were subjected to adhesion tests and corrosion tests according to quality regulations prescribed GSB and Qualitysteelcoat: Adhesion Cross cut adhesion pull-off EN ISO 16276-2; ASTM D3359

[0038] Adhesion Reversed impact ASTM D2794 or EN ISO 6272-1 and

[0039] Corrosion tests: Accelerated corrosion testing according to ASTM B117 Neutral Salt Spray for iron, iron alloys and zinc coated steels . Tables 2 -4 summarize the test results.

Table 1. Examples composition

Example	Chromium compound (source)	Concentration [Cr] g/L	Fluoride source	Molair ratio Cr : F	Organic corrosion inhibitor (content mg/L)	Surfactant	Watersoluble polymer (content, mg/L)	pH
Ex1	dissolved CrF3*4aq	1,5	CrF3*4aq	1 :3	divalent, phthalate (200)		PAA (200)	3.4
Ex2	dissolved CrF3*4aq	1,5	CrF3*4aq	1 :3	divalent, phthalate (200)	Plurafac LF	PAA (200)	3.4
Ex3	Cr(III), Fluoride	4	HF	1 :3	Dodicor (200)	Plurafac LF	PAA (200)	3.3
Ex4	Cr(III), Fluoride	4	HF	1 :3	Dodicor (200)			3.3
Ex5	Cr(III), Fluoride	4	HF	1 :3	divalent, phthalate (200)			3.0
Ex6	Cr(III), Fluoride	4	HF	1: 3	propargyl alcohol (20)			2.9
Comp 1	dissolved CrF3*4aq	1,5	CrF3*4aq	1 :3			PAA (200)	3.0
Comp 2	Cr(III), Fluoride	0,28	HF	1 : 3				3.1
Comp 3	Cr(III), Fluoride	4	HF + ABF	2 :7				3.4
Comp 4	Cr(III), Fluoride	4	HF	1 :3		Plurafac LF	PAA(100), PVA (50)	3.0
Comp 5	DiChromiumTriSulphate	4	H2ZrF6	1 :6	caprylic acid (50)			3.0
Comp 6								
Comp 7	Cr(III), Fluoride	4	HF	1 :3			PAA (100), PVA (50)	2.9
Comp 8								

HF Hydrogen Fluoride
ABF Ammonium bi Fluoride
$CrF_3.4H_2O$ Chromium Trifluoride
H_2ZrF_6 HexafluoroZirconium Acid
Dodicor (Clariant) commercial blend of corrosion inhibitors: benzyl quaternary amine imidazoline salt and propynol
Plurafac LF (BASF) commercial branched and linear ethoxylated fatty alcohol
PAA Poly acrylic acid (Mw = 100000 g/mol)
PVA Poly vinyl alcohol (Mw = 60000 g/mol)

Tabel 2. Examples method and results

Examples	Metal substrate	Pretreatment	Application room temperature	Discoloration / flash rust during unforced drying	Coating wt (mg Cr/m2)	Type of organic coating	Adhesion test #cut impact	<2mm Corrosion after x hours
Ex5	CRS	alk cleaned	immersion 3 min	no flash rust	80	coil coat	pass	500
Comp 1	CRS	alk cleaned	immersion 3 min	slightly yellow stains	50	coil coat	pass	n/a
Comp 2	CRS	alk cleaned	immersion 3 min	yellow/ orange stains	40	coil coat	failed	n/a
Comp 3	CRS	alk cleaned	immersion 3 min	slightly yellow stains	120	coil coat	pass	240
Comp 4	CRS	alk cleaned	immersion 3 min	slightly yellow stains	60	coil coat	pass	240
Comp 5	CRS	alk cleaned	immersion 3 min	no flash rust	40	coil coat	failed	<168
Ex6	C-steel	grid blasted	spray 2 min	no flash rust	90	epoxy powder	pass	1000
Comp 6	C-steel	grid blasted		no flash rust		epoxy powder	pass	<500
Comp 7	C-steel	grid blasted	spray 2 min	slightly yellow stains	75	powder	pass	500
Comp 8	C-steel	grid blasted		no flash rust		powder	pass	<240

CRS Oiled cold rolled steel
C steel Low carbon steel DC-1
alkaline cleaned alkaline cleaning (pH =10) during 3 minutes at 52 °C
grid blasted mechanical roughening and removal of rust and oxides
coil coat liquid polyester coating (7 micrometres)cured at 240° C in 40 - 60 seconds
epoxy powder epoxy primer powder coating (300 micrometres) cured at room temperature in 2 weeks
powder powder coating (80 micrometres) cured at 175oC in 15 minutes
corrosion test SST is neutral salt spray test according to ASTM B117

Table 3: Test results

Carbon steels with mill scale or rusted/oxidized surfaces											
Example	Inv	Com p	Comp	Inv	Comp	Inv	Comp	Inv	Comp	Inv	Comp
Mechanical removal of rust and mill scale											
Dry abrasive grit blast cleaniing	x	x	x	x		x	x			x	x
Scuffing disc/followed by grit blasting								x	x		
Chemical Treatment											
Commercial alkaline cleaned surface	x	x			x						
Commercial iron phosphated surface	x	x			x						
Ex1 spray application (2 min)	x			x						x	
Ex2 wipe application						x		x			
Commercial Zr treated spray application					x						
Organic Coating											
Type	wet	wet	powder	powder	powder	wet	wet	wet	wet	powder	powder
Coating thickness (μm)	95	95	60	60	60	1500	1500	1500	1500	90	90
Adhesion test											
Adhesion cross-cut 1 mm + tape											
Corrosion											
NEN en ISO 92227 Neutral Salt Spray Test (ASTM B117)											
Creepage from the scribe (ISO 4628-8)											
After 500 hrs exposure (mm)			4	0	>50	1.5	3.4	2.3	3.7		
After 1000 hrs exposure (mm)	3	>20								2	14

Table 4. Test results

	Slightly oiled mild steel substrate without oxide/mill scale						
Without solvent degreasing	x				x	x	x
Solvent degreasing by wiping		x	x	x			
Wipe/brush application of treatment compostion							
Comp 7			x				
Comp 4				x	x		
Ex5						x	
Ex3							x
Properties after treatment							
Wetting pretreatment	n/a	n/a	poor	good	good	poor	good
Flash rust during drying	no	no	yes	yes	yes	no	no
Wetting of powder paint (100 μm)	very poor	poor	good	good	good	good	good

[0040] From the above examples and test results it appears that the compositions according to the invention present better performance with respect to coating adhesion, wettability, flash rust inhibition and corrosion resistance than the comparative examples, that fail in one or more of these aspects or are worse.

Claims

1. A method of treating a metal surface of iron or iron alloy for providing corrosion protection, adhesion of coating and/or adhesive, which method comprises the application of an aqueous composition onto the metal surface of iron or iron alloy,
which composition consists of:

trivalent chromium (Cr^{3+}):	1.16-7.0	g/l
total fluoride (F^-):	1.3-7.7	g/l
organic corrosion inhibitor:	up to 2.0	g/l
water soluble polymers:	0-4.0	g/l
water soluble surfactant	0-1.0	g/l
organo functional silane and/or oligomer	0-4.0	g/l
pH adjusting agent	0-1.0	g/l
fluoride adjusting agent	0-1.0	g/l

wherein the molar ratio of Cr^{3+} to F^- ranges from 0.25-0.4, and wherein the pH ranges from 2.0-4.4.

2. The method according to claim 1, wherein the concentration trivalent chromium (Cr^{3+}) in the aqueous composition is in the range of 3.0-6.0 g/L.

3. The method according to claim 1 or 2, wherein the mol ratio Cr^{3+}: F- in the aqueous composition is in the range of 0.30-0.36, preferably 0.32-0.34 and more preferably 1:3.

4. The method according to any one of the preceding claims, wherein the composition comprises dissociated $CrF_3.4H_2O$.

5. The method according to any one of the preceding claims, wherein the concentration organic corrosion inhibitor in the aqueous composition is in the range of 0.0001-2.0, preferably 0.1-1.0 g/L.

6. The method according to any one of the preceding claims, wherein the concentration of the water soluble polymers

in the aqueous composition ranges from 0.01-4.0, preferably 0.1-1.0 g/L.

7. The method according to any one of the preceding claims, wherein the concentration of the water soluble surfactant in the aqueous composition is in the range of 0.001-0.5, preferably 0.01-0.1 g/L.

8. The method according to any one of the preceding claims, wherein the pH ranges from 2.7-3.8, preferably from 2.7 to 3.4.

9. The method according to any one of the preceding claims, wherein the coating weight, measured by XRF after drying, is in the range of 20-200 mg chromium/m^2.

10. The method according to any one of the preceding claims, wherein the metal surface is selected from a solvent degreased metal surface of iron or iron alloy, a metal surface of iron or iron alloy from which scale and oxides have been removed mechanically, a metal surface of iron or iron alloy that has already been provided with a phosphate conversion coating, and an oiled metal surface of iron and iron alloy that is free from scale and oxides.

11. An aqueous composition for treating a metal surface of iron or iron alloy, in particular for use in the method according to any one of the preceding claims, which composition consists of:

trivalent chromium (Cr^{3+}):	1.16-7.0	g/l
total fluoride (F^-):	1.3-7.7	g/l
organic corrosion inhibitor:	up to 2.0	g/l
water soluble polymers:	0-4.0	g/l
water soluble surfactant	0-1.0	g/l
organo functional silane and/or oligomer	0-4.0	g/l
pH adjusting agent	0-1.0	g/l
fluoride adjusting agent	0-1.0	g/l

wherein the molar ratio of Cr^{3+} to F^- ranges from 0.25-0.4, and wherein the pH ranges from 2.0-4.4.

12. The composition according to claim 11, wherein the concentration trivalent chromium (Cr^{3+}) is in the range of 3.0-6.0 g/L

13. The composition according to claim 11 or 12, wherein the mol ratio Cr^{3+}: F- is in the range of 0.30-0.36, preferably 0.32-0.34 and more preferably 1:3.

14. The composition according to any one of the preceding claims 11-13, wherein the concentration organic corrosion inhibitor is in the range of 0.0001-2.0, preferably 0.1-1.0 g/L.

15. The composition according to any one of the preceding claims 11-14, wherein the concentration of the water soluble polymers in the aqueous composition ranges from 0.01 - 4.0, preferably 0.1-1.0 g/L; and/or the concentration of the water soluble surfactant in the aqueous composition is in the range of 0.001-0.5, preferably 0.01-0.1 g/L; and/or the pH is in the range of 2.7-3.8, preferably 2.7-3.4.

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EUROPEAN SEARCH REPORT

Application Number
EP 17 18 8548

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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