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(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: 0-2,0 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.

P32818NL00/JV

METHOD OF TREATING METAL SURFACES WITH AN AQUEOUS COMPOSITION AND AQUEOUS COMPOSITION

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

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 improve adhesion, when chemical treatment steps were not practical to apply. Only cleaning or mechanical treatment of metal parts made of especially iron and iron alloys without any suitable chemical treatment will result in flash rusting, if the parts are not painted within a few hours. 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..

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.

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

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

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.

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.

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.

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.

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..

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

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.

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.

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:	0-2,0	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.

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

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.. Metal surfaces that can be suitably treated with the composition according to the invention include iron, 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 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.

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 waive a conventional paint primer. Additionally, the layer thickness can be less than that of a conventional primer.

Trivalent chromium is present in amount of 1.16-1.7.0 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 0.30-0.36, 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 characteristics.

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.

The pH ranges from 2.0-4.4, preferably 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.

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.

The composition according to the invention may additionally comprise 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. 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.

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..

Other 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. If the amount of surfactant is too high, it can cause excessive foaming in the process.

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.

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 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 and abrading. Chemical pre-treatment include (acidic/alkaline) 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.

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.

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.

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.

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

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

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.

Aqueous metal surface treatment liquids having a composition as indicated in Table 1 were prepared and applied to metal surfaces as indicated in Table 2..

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

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

Corrosion tests: Accelerated corrosion testing according to ASTM B117 Neutral Salt Spray for iron, iron alloys and zinc coated steels . Tables 2 and 3 summarize the test results.

It appears that the examples according to the invention passed the adhesion test and had a significant better performances regarding corrosion than the comparative examples.

Tabel 1. Examples composition

Example	Chromium compound	Concentration [Cr] g/l	Fluoride source	Molar ratio Cr :F	Additive	Concentration [additive] mg/l	pH
3	dissolved CrF3*4aq	1.5	CrF3*4aq,	1 : 3	PAA	200	3.0
Comp 3	dissolved CrF3*4aq	0.28	CrF3*4aq	1 : 3	PAA	2500	3.1
4	Cr(III) Fluoride	4	HF + ABF	2 : 7			3.4
Comp 4	None						
5	Cr(III) Fluoride	4	HF	1 : 3			3.0
Comp 5	Di Chromium TriSulphate	4	H2ZrF6	1 : 6	caprylic acid	350	3.0
6	Cr(III) Fluoride	4	HF	1 : 3	zinc phthalate	200	3.0
Comp 6	Cr(III) Fluoride	4	HF	1 : 3	benzotriazole	200	3.0
7	Cr(III) Fluoride	4	HF	1: 3	propargyl alcohol	20	2.9
Comp 7	Nonet						
8	Cr(III) Fluoride	4	HF	1 : 3	PAA, PVA	250	2.9
Comp 8	None						

HF	Hydrogen Fluoride
ABF	Ammonium bi Fluoride
$CrF_3.4H_2O$	Chromium Trifluoride
H_2ZrF_6	HexafluoroZirconium Acid
PAA	Poly acrylic acid
PVA	Poly vinyl alcohol

Tabel 2. Examples method

Example	Metal substrate	Pre-treatment	Application (time)	Coating weight mg Cr/m^2	Type of organic coating	Adhesion tape test on cross cut and reversed impact	< 2mm corrosion after x hours
3	CRS	alkaline cleaned	immersion 3 min	50	coil coat	pass	NA
Comp 3	CRS	alkaline cleaned	immersion 3 min	40	coil coat	failed	NA
4	CRS	alkaline cleaned	immersion 3 min	120	coil coat	pass	240
Comp 4	CRS	alkaline cleaned	phosphating		coil coat	pass	<168
5	CRS	alkaline cleaned	immersion 3 min	60	coil coat	pass	<240
Comp 5	CRS	alkaline cleaned	immersion 3 min	40	coil coat	failed	<168
6	CRS	alkaline cleaned	immersion 3 min	80	coil coat	pass	500
Comp 6	CRS	alkaline cleaned	immersion 3 min	250	coil coat	failed	<336
7	C-steel	grid blasted	spray 2 min	90	epoxy liquid	pass	1000
Comp 7	C-steel	grid blasted	no treatment		epoxy liquid	pass	<500
8	C-steel	grid blasted	spray 2 min	75	powder	pass	500
Comp 8	C-steel	grid blasted	no treatment		powder	pass	<240

CRS	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 240oC in 40 - 60 seconds
epoxy liquid	epoxy primer (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

CRS sheet treated at different concentrations and immersion times, coil coating paint cured at 240 °C was applied resulting in 7 micrometres dry coating thickness				
Concentration [Cr] g/L	**Immersion time seconds**	**Adhesion cross cut and reversed impact**	**pH**	**Comment**
11	3	fail	2.9	process time is not feasible in practice
11	30	fail	2.9	
11	180	fail	2.9	
5.5	3	pass	3	process time is not feasible in practice
5.5	30	pass	3	
5,5	180	pass	3	
2.8	3	pass	3.1	process time is not feasible in practice
2.8	30	pass	3.1	
2.8	180	pass	3.1	
0.28	3	pass	3.4	process time is not feasible in practice
0.28	30	fail	3.4	
0.28	180	fail	3.4	

C O N C L U S I E S

1. Werkwijze voor het behandelen van een metalen oppervlak van ijzer of ijzerlegering, voor corrosiebescherming, hechting van een bekleding en/of lijm, die het aanbrengen van een waterige samenstelling op het metalen oppervlak van ijzer of ijzerlegering omvat, welke samenstelling bevat:

driewaardig chroom (Cr^{3+}):	1,16-7,0	g/l
totaal fluoride (F^-):	1,3-7,7	g/l
organische corrosie inhibitor:	tot aan 2,0	g/l
wateroplosbare polymeren:	0-4,0	g/l
wateroplosbaar oppervlakte-actief middel	0-1,0	g/l
organofunctioneel silaan en/of oligomeren:	0-4,0	g/l
pH instelmiddelen	0-1,0	g/l
fluoride instelmiddelen	0-1,0	g/l

waarbij de molverhouding Cr^{3+}:F^- ligt in het gebied van 0,25-0,4, en waarbij de pH ligt in het gebied van 2,0-4,4.

2. Werkwijze volgens conclusie 1, waarbij de concentratie driewaardig chroom (Cr^{3+}) in de waterige samenstelling ligt in het gebied van 3,0-6,0 g/l.

3. Werkwijze volgens conclusie 1 of 2, waarbij de molverhouding Cr^{3+}:F^- in de waterige samenstelling ligt in het gebied van 0,30-0,36 bij voorkeur van 0,32-0,34 en meer bij voorkeur 1:3 is.

4. Werkwijze volgens een van de voorgaande conclusies, waarbij de samenstelling gedissocieerd $CrF_3.4H_2O$ bevat.

5. Werkwijze volgens een van de voorgaande conclusies, waarbij de concentratie organische corrosie inhibitor in de samenstelling 0,0001-2,0, bij voorkeur 0,1-1,0 g/l bedraagt.

6. Werkwijze volgens een van de voorgaande conclusies, waarbij de concentratie wateroplosbare polymeren in de samenstelling ligt in het gebied van 0,01-4,0, bij voorkeur van 0,1-1 g/l.

7. Werkwijze volgens een van de voorgaande conclusies, waarbij de concentratie wateroplosbaar oppervlakte-actief middel in de samenstelling ligt in het gebied van 0,001-0,5, bij voorkeur 0,01-0,1 g/l.

8. Werkwijze volgens een van de voorgaande conclusies, waarbij de pH ligt in het gebied van 2,7-3,4.

9. Werkwijze volgens conclusie een van de voorgaande conclusies, waarbij het bekledingsgewicht in het gebied van 20-200 mg chroom/m^2 ligt, gemeten met XRF na drogen.

10. Werkwijze volgens een van de voorgaande conclusies, waarbij het metalen oppervlak een reeds van een fosfaat conversie bekleding voorzien metalen oppervlak van ijzer of ijzerlegering is.

11. Waterige samenstelling voor het behandelen van een metalen oppervlak van ijzer of ijzerlegering, in het bijzonder voor toepassing bij de werkwijze volgens een van de voorgaande conclusies, welke samenstelling bevat:

driewaardig chroom (Cr^{3+}):	1,16-7,0	g/l
totaal fluoride (F^-):	1,3-7,7	g/l
organische corrosie inhibitor:	tot aan 2,0	g/l
wateroplosbare polymeren:	0-4,0	g/l
wateroplosbaar oppervlakte-actief middel	0-1,0	g/l
organofunctioneel silaan en/of oligomeren:	0-4,0	g/l
pH instelmiddelen	0-1,0	g/l
fluoride instelmiddelen	0-1,0	g/l

waarbij de molverhouding Cr^{3+}:F^- ligt in het gebied van 0,25-0,4, en
waarbij de pH ligt in het gebied van 2,0-4,4.

12. Samenstelling volgens conclusie 11, waarbij de concentratie driewaardig chroom (Cr^{3+}) ligt in het gebied van 3,0-6,0 g/l.

13. Samenstelling volgens conclusie 11 of 12, waarbij de molverhouding Cr3+:F- ligt in het gebied van 0,30-0,36 bij voorkeur van 0,32-0,34 en meer bij voorkeur 1:3 is.

14. Samenstelling volgens een van de voorgaande conclusies 11-13, die gedissocieerd CrF3.4H2O bevat.

15. Samenstelling volgens een van de voorgaande conclusies 11-14, waarbij de concentratie organische corrosie inhibitor 0,0001-2,0, bij voorkeur 0,1-1,0 g/l bedraagt.

16. Samenstelling volgens een van de voorgaande conclusies 11-15, waarbij de concentratie wateroplosbare polymeren ligt in het gebied van 0,01-4,0, bij voorkeur van 0,1-1 g/l.

17. Samenstelling volgens een van de voorgaande conclusies 11-16, waarbij de concentratie wateroplosbaar oppervlakte-actief middel ligt in het gebied van 0,001-0,5, bij voorkeur 0,01-0,1 g/l.

18. Samenstelling volgens een van de voorgaande conclusies 11-17, waarbij de pH ligt in het gebied van 2,7-3,4.

ABSTRACT

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:	0-2,0	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.

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE
	P32818NL00/JV
Nederlands aanvraag nr. **2017398**	Indieningsdatum **31-08-2016**
	Ingeroepen voorrangsdatum
Aanvrager (Naam) **AD Productions B.V.**	
Datum van het verzoek voor een onderzoek van internationaal type **17-09-2016**	Door de Instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. **SN67354**

I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)

Volgens de internationale classificatie (IPC)

C23C22/34;C23C22/83

II. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimumdocumentatie

Classificatiesysteem	Classificatiesymbolen
IPC	**C23C**

Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

III.	☐ **GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES**	(opmerkingen op aanvullingsblad)
IV.	☐ **GEBREK AAN EENHEID VAN UITVINDING**	(opmerkingen op aanvullingsblad)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2017398

A. CLASSIFICATIE VAN HET ONDERWERP
INV. C23C22/34 C23C22/83
ADD.

Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimum documentatie (classificatie gevolgd door classificatiesymbolen)
C23C

Onderzochte andere documentatie dan de minimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)
EPO-Internal, WPI Data

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie *	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	EP 0 111 897 A1 (COLLARDIN GMBH GERHARD [DE]) 27 juni 1984 (1984-06-27) * conclusies *	1-18
X	EP 0 337 411 A2 (UNILEVER NV [NL]; UNILEVER PLC [GB]) 18 oktober 1989 (1989-10-18) * conclusies; voorbeeld 1 *	11
A	US 2005/103229 A1 (TANAKA KAZUYA [JP] ET AL) 19 mei 2005 (2005-05-19) * alineas [0005] - [0035]; conclusies * * voorbeelden A, primer 8 *	1-18
A	US 2011/100513 A1 (SCHLOSSER TED M [US] ET AL) 5 mei 2011 (2011-05-05) * conclusies; voorbeeld 1 *	1-18

☐ Verdere documenten worden vermeld in het vervolg van vak C.

☒ Leden van dezelfde octrooifamilie zijn vermeld in een bijlage

* Speciale categorieën van aangehaalde documenten

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft

"D" in de octrooiaanvrage vermeld

"E" eerdere octrooi(aanvrage), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven

"L" om andere redenen vermelde literatuur

"O" niet-schriftelijke stand van de techniek

"P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur

"T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvrage, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding

"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur

"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht

"&" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid	Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type
17 mei 2017	

Naam en adres van de instantie	De bevoegde ambtenaar
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Mauger, Jeremy

Formulier PCT/ISA/201 (tweede blad) (Januari 2004)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar de stand van de techniek: NL 2017398

In het rapport genoemd octrooigeschrift	Datum van publicatie	Overeenkomend(e) geschrift(en)		Datum van publicatie
EP 0111897	A1 27-06-1984	AU 557724	B2	08-01-1987
		BR 8306981	A	31-07-1984
		CA 1219790	A	31-03-1987
		DE 3247729	A1	05-07-1984
		EP 0111897	A1	27-06-1984
		ES 8406563	A1	01-11-1984
		GR 79449	B	30-10-1984
		JP H076071	B2	25-01-1995
		JP S59133373	A	31-07-1984
		MX 7298	E	26-04-1988
		NO 834243	A	25-06-1984
		US 4761189	A	02-08-1988
		ZA 8309574	B	29-08-1984
EP 0337411	A2 18-10-1989	DD 280557	A5	11-07-1990
		DE 3812076	A1	26-10-1989
		EP 0337411	A2	18-10-1989
		YU 71689	A	31-12-1990
US 2005103229	A1 19-05-2005	AU 2003201868	A1	30-07-2003
		CN 1615375	A	11-05-2005
		JP 4081276	B2	23-04-2008
		JP 2003201576	A	18-07-2003
		KR 20040074115	A	21-08-2004
		US 2005103229	A1	19-05-2005
		WO 03060190	A1	24-07-2003
US 2011100513	A1 05-05-2011	US 2011100513	A1	05-05-2011
		US 2015322575	A1	12-11-2015
		WO 2011056944	A1	12-05-2011

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
SN67354	31.08.2016		NL2017398

International Patent Classification (IPC)
INV. C23C22/34 C23C22/83

Applicant
AD Productions B.V.

This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the application
- ☒ Box No. VIII Certain observations on the application

	Examiner
	Mauger, Jeremy

Application number

WRITTEN OPINION

NL2017398

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	2, 4, 5, 7, 10, 12, 14, 15, 17
	No:	Claims	1, 3, 6, 8, 9, 11, 13, 16, 18
Inventive step	Yes:	Claims	
	No:	Claims	1-18
Industrial applicability	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations

see separate sheet

WRITTEN OPINION

Box No. VII Certain defects in the application

see separate sheet

Box No. VIII Certain observations on the application

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following documents:

D1	EP 0 111 897 A1 (COLLARDIN GMBH GERHARD [DE]) 27 juni 1984 (1984-06-27)
D2	EP 0 337 411 A2 (UNILEVER NV [NL]; UNILEVER PLC [GB]) 18 oktober 1989 (1989-10-18)
D3	US 2005/103229 A1 (TANAKA KAZUYA [JP] ET AL) 19 mei 2005 (2005-05-19)
D4	US 2011/100513 A1 (SCHLOSSER TED M [US] ET AL) 5 mei 2011 (2011-05-05)

2 Document D1 (see claims) discloses a conversion coating process and solution for treating steel or aluminium surfaces. The solution contains 0.5-10 g/l Cr(III), 0.55-11 g/l F, 0.6-12.5 g/l PO_4 and 0.15-5.0 g/l of an organic film-forming agent (notably a water-soluble acrylic polymer, such polymers are also corrosion inhibitors). The Cr(III) and F are preferably added as CrF_3, but the Cr:F ratio can vary between 1:2.5 to 1:3.5 (0.4 to 0.28). The pH is 2-3 and preferably 5-100 mg/m2 of chromium are deposited on the metal surface.

2.1 The composition used in claim 1 and defined in claim 11 does not exclude that further components such as phosphate ions are present. The concentrations of chromium, fluoride and film-forming agent furthermore have such a large overlap with those now claimed that no novel selection can be recognised and thus document D1 is considered to be novelty destroying for the subject-matter of claims 1, 3, 6, 8, 9, 11, 13, 16 and 18.

2.2 The subject-matter of the remaining claims is not considered to be inventive. The chromium concentration in claims 2 and 12 corresponds to the centre of the range in document D2 and appears to result in no clear advantages. The use of $CrF_3.4H_2O$ as the source of chromium (claims 4 and 14) is obvious as this compound is more soluble than the other chromium (III) fluorides. The preferred film-forming agent (a polyacrylate) can also be a corrosion inhibitor and thus this component also renders claims 5 and 15 obvious. The addition of surfactants to such compositions (claims 7 and 17) to ensure a more even

film formation is routine and not inventive. Chromium (III) solutions are known to useful as passivating rinses for phosphated surfaces and thus the process of claim 10 is also not inventive.

3 Document D2 (see example 1 and claims) discloses a conversion coating liquid for zinc surfaces. In example 1 a concentrate was prepared containing 50g/l $Cr(III)Cl_3$, 125 g/l $NaNO_3$ and 50 g/l NaF. This concentrate was diluted by a factor 10 and used to treat zinc. The diluted bath had a pH of 2.0, contained 1.64 g/l Cr (III) (0.032 M) and 2.2 g/l F (0.12 M). The molar ratio of Cr/F was thus 0.27. The diluted bath although not used for iron or steel surfaces is clearly suitable for this use and thus this document is novelty-destroying for claim 11.

Re Item VII

Certain defects in the application

1 The relevant background art disclosed in document D1 is not mentioned in the description, nor is this document identified therein.

Re Item VIII

Certain observations on the application

1 It is clear from the examples on pages 7-10 that feature of claim 9 is essential to the definition of the process of the invention. Example 6 and comparative example 6 both use compositions in accordance with claim 1, but on the process of example 6, which had a chromium coating weight in the range of claim 9, solved the problem (good corrosion protection and paint adhesion.

Since independent claim 1 does not contain this feature it does not meet the requirement of clarity that any independent claim must contain all the technical features essential to the definition of the invention.

2 The term "organic corrosion inhibitor" as used in claim 1, is not considered to be clear, because a skilled person cannot determine from the term, which compounds may or may not be used. A compound may be a corrosion inhibitor or not depending upon the corrosive environment a metal is exposed to and thus the term does not clearly indicate, which compounds may be used.