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(54) METHOD FOR MANUFACTURING CHROMIUM-CHROMIUM OXIDE COATED BLACKPLATE

(57) This invention relates to a method for electroplating uncoated blackplate with a plating layer and an improvement thereof. The invention also relates to a method wherein the coated blackplate is further coated on one or both sides by a film lamination step or a direct extrusion step, and to the use of said coated blackplate in a process to produce containers for packaging purposes.

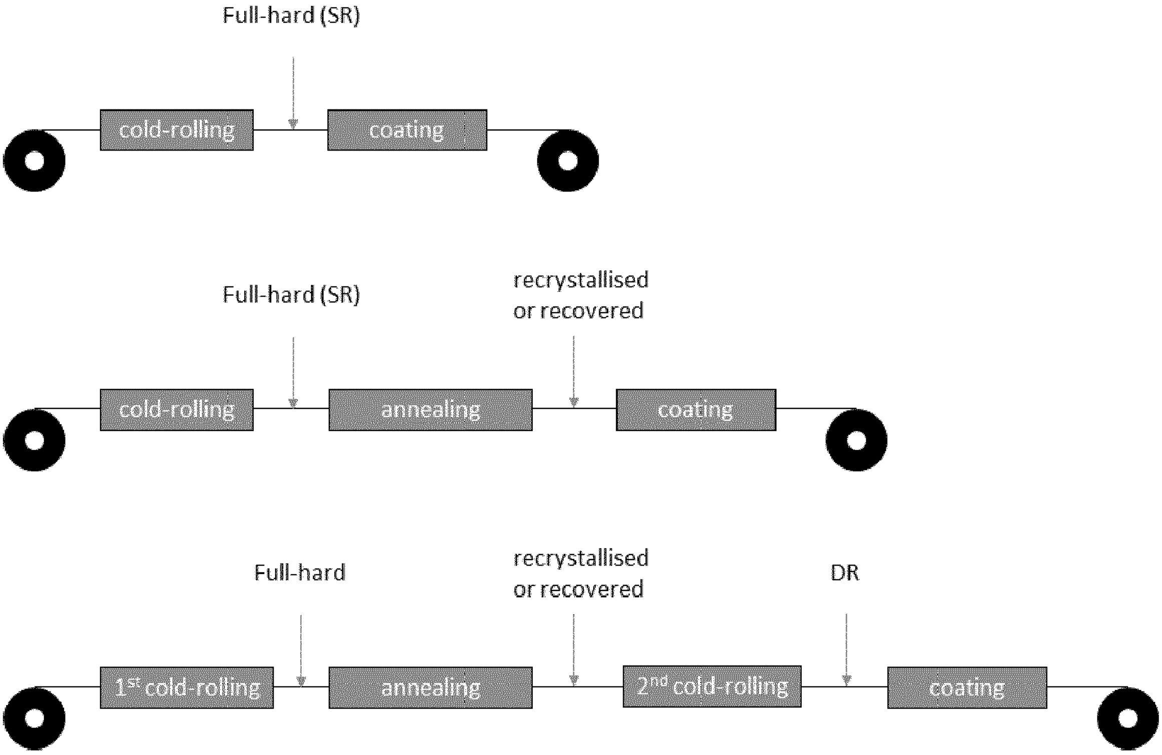

FIGURE 1

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Description

[0001] This invention relates to a method for electroplating an uncoated steel strip with a plating layer and an improvement thereof.

[0002] In continuous steel strip plating, a cold-rolled steel strip is provided which is usually annealed after cold-rolling to soften the steel by recrystallisation annealing or recovery annealing. After the annealing and before plating the steel strip is first cleaned for removing oil and other surface contaminants. After the cleaning step, the steel strip is pickled in a sulphuric or hydrochloric acid solution for removing the oxide film. Between different treatment steps the steel strip is always rinsed with deionised water to prevent contamination of the solution used for the next treatment step with solution of the preceding treatment step. Consequently the steel strip is thoroughly rinsed after the pickling step. During rinsing and transport of the steel strip to the plating section a fresh thin oxide layer is formed instantly on the bare steel surface and needs to be protected quickly.

[0003] One such process used in electroplating is called electrodeposition. The part to be plated (the steel strip) is the cathode of the circuit. The anode of the circuit may be made of the metal to be plated on the part (dissolving anode, such as those used in conventional tinplating) or a dimensionally stable anode (which does not dissolve during plating). The anode and cathode are immersed in an electrolyte solution containing ions of the metal to be deposited onto the blackplate substrate.

[0004] Blackplate is a tin mill product which has not (yet) received any metallic coating during production. It is the basic material for the production of other tin mill products. Blackplate can be single reduced (SR) full-hard or annealed (recovery annealed or recrystallisation annealed) or double reduced (DR) in which case it has been subjected to a second cold rolling reduction after annealing. The SR or DR blackplate is usually provided in the form of a coiled strip and is the uncoated starting material for the coating process according to the invention. Figure 1 schematically summarises the process steps to obtain the coated product, starting from a hot-rolled strip. Before cold-rolling, the hot-rolled strip is usually pickled (not shown) to remove the hot-rolling scale and cleaned (not shown) to remove any contaminants from the strip.

[0005] In the production of packaging steels with an electroplated chromium coating from an electrolyte solution comprising a trivalent chromium compound on an uncoated steel strip (blackplate), as disclosed in WO2014202316-A1 it occurs occasionally that at lower line speeds, the resulting coated product has a stripy appearance. Although the stripes are very faint and cannot be detected with XPS and/or SEM, they are nevertheless visible with the naked eye. The pattern appears to be even more visible when a clear lacquer coating (thermosetting coating) or polymer coating (thermoplastic coating) is applied onto the coated product. Although the coated product performs just as well in terms of corrosion performance, coatability, adherence of the lacquer coating or polymer coating to the coated product and the can-making performance of the coated product, no adverse effects have been observed of the presence of the stripes, the stripy appearance is considered to be visually less appealing and therefore undesired.

[0006] It is the object of the invention to improve the surface appearance of an electroplated chromium coating from an electrolyte solution comprising a trivalent chromium compound on an uncoated (blackplate) steel strip.

[0007] The object is reached with a method for manufacturing a chromium metal - chromium oxide coated blackplate by electrolytically depositing the chromium metal - chromium oxide coating on blackplate in a continuous high speed plating line operating at a line speed of at least 50 m/min from an electrolyte solution comprising a trivalent chromium compound, wherein the electrolyte solution is free of chloride ions and free of a boric acid buffering agent, the electrically conductive substrate acts as a cathode and an anode comprising a catalytic coating of iridium oxide or a mixed metal oxide for reducing or eliminating the oxidation of Cr^{3+}-ions to Cr^{6+}-ions, wherein the electrolyte solution contains at most 250 mM Cr^{3+}-ions, a complexing agent at a (complexing agent/Cr^{3+}) molar ratio of at least 1:1, 0 to 2800 mM of sodium sulphate (Na_2SO_4), a pH of between 1.5 and 3.0 measured at 25°C, and wherein the plating temperature is between 30 and 70 °C.

[0008] Preferable embodiments are provided in the dependent claims. For the sake of clarity it is noted that 1 mM means 1 millimole/l.

[0009] Firstly, it is noted that the process according to the invention is equally applicable to provide a chromium metal-chromium oxide coating on other metal substrates such as nickel plated steel strip.

[0010] Secondly, if the pH of the electrolyte solution becomes too high or too low, then sulphuric acid or sodium hydroxide may be added to adjust the pH to a value inside the desired range. Also different acids or bases may be used, but in view of the bath chemistry sulphuric acid and sodium hydroxide are preferable.

[0011] Thirdly, as blackplate any steel grade suitable for producing packaging steel may be used. By means of example, but not intended to be limited by this, reference is made to the steel grades for packaging applications in EN10202:2001.

[0012] A stripy appearance of a deposited surface is usually associated with a certain inhomogeneity in the electroplating process. A local difference in coverage or local differences in the composition of the coating layer may be the cause of the stripy appearance. It would be obvious to the skilled person to attempt to solve this problem by increasing the amount of deposited material by either increasing the amount of metal ions in the electrolyte, or by increasing the current density. WO2014202316-A1 discloses a Cr^{3+} electrolyte using 120 g/l (= 385 mM) basic chromium(III)sulphate. This resulted in the aforementioned stripy surface under some conditions, such as a low line speed. Surprisingly, the inventors found that by increasing the chromium(III) content in the electrolyte, the appearance of the coated strip worsened, and that the stripy appearance persisted. Surprisingly and counter-intuitively the inventors found that decreasing the amount of metal ions in the electrolyte resulted in a decrease in the stripy surface and that the surface becomes even and shiny when the coating was deposited in accordance with the process of the invention.

[0013] The reduction of the pH of the electrolyte also appeared to have a beneficial effect on the surface appearance of the coated product. This also is counter-intuitive, because a lower pH decreases the efficiency of this particular plating process. The higher the pH of the electrolyte, the lower the current density that is needed to deposit a certain amount of chromium. An increase of 2.7 to 2.85 already results in a considerable increase in current density required for a certain plating thickness (as expressed in mg/m^2). This effect is independent of the line speed, although the magnitude of the current density required for a certain plating thickness increases with increasing line speed. So also at higher line speeds, a lower pH results in a less efficient plating process. And, reducing the pH has a positive effect on the appearance of the coated blackplate in that the stripy appearance is absent.

[0014] The effect of a lower chromium content in the electrolyte solution is shown in Figure 2. The lower the chromium content, the lower the current density needed for a certain plating thickness.

[0015] In a preferred embodiment the complexing agent is formate ($HCOO^-$), added to the electrolyte solution preferably as sodiumformate (HCOONa). Other complexing agents that can be used instead of formate, or in addition thereto are oxalate-ions, and acetate-ions.

[0016] In an embodiment wherein the Cr^{3+}-ions are provided by a water soluble chromium(III) salt and wherein the water soluble chromium(III) salt preferably is one or more of the following water soluble chromium(III) salts:

- basic chromium(III)sulphate
- chromium(III)formate
- chromium(III)oxalate
- chromium(III)acetate.

[0017] These salts have proven to work well in the eletrolyte as claimed. The use of basic chromium(III)sulphate and/or chromium(III)formate is preferable from the point of view of keeping the bath chemistry as simple as possible. The addition of these compounds does not introduce additional ion-types to the electrolyte. The use of the chromium(III)oxalate and/or chromium(III)acetate instead of, or in addition to, chromium(III)formate may be desired if a different complexing agent is needed.

[0018] In an embodiment the electrolyte solution contains at most 225 mM of Cr^{3+}-ions and/or at least 100 mM of Cr^{3+}-ions, preferably at least 125 mM of Cr^{3+}-ions. This preferred range provides good results.

[0019] In an embodiment the pH of the electrolyte solution is at most 2.8, preferably at most 2.6 or 2.4, more preferably at most 2.2. Although the lower pH results in a less efficient plating process, the surface quality is much improved in that it shows no stripes.

[0020] In an embodiment the formate/Cr^{3+} molar ratio is at most 2.5:1. The formate-ion is needed as a complexing agent and the ratio of at most 2.5:1 has proven to be sufficient in most cases. More preferably the molar ratio is at most 2.0:1, even more preferably 1.75:1. Preferably the molar ratio is at least 1.1:1, more preferably 1.25:1.

[0021] In an embodiment the electrolyte solution contains at least 75 mM and/or at most 600 mM of sodium formate. When using only sodium formate as the addition of formate, and no chromium(III)formate as the water soluble chromium salt, then at least 75 mM should be added, preferably at least 100 mM and even more preferably 200 mM. The maximum is preferably at most 600 mM of sodium formate. If also chromium(III)formate is added to the electrolyte solution as the water soluble chromium salt then the formate added this way needs to be subtracted from the sodium formate additions as given herein above. For example, if 50 mM of formate is added as chromium(III)formate, then the values for sodium formate become at least 25 mM, preferably at least 50 mM and even more preferably 150 mM. The maximum is preferably at most 550 mM of sodium formate.

[0022] In an embodiment the electrolyte solution contains at least 210 mM and/or at most 845 mM of sodium sulphate.

[0023] In a preferred embodiment the plating temperature is at least 40 °C, preferably at least 50 °C, more preferably at least 55 °C.

[0024] In an embodiment the line speed of the plating line is at least 100 m/min, more prefebrably at least 200 m/min.

[0025] In an embodiment the coated blackplate is further coated on one or both sides by a film lamination step or a direct extrusion step, with an organic coating consisting of a thermoplastic single layer, or a thermoplastic multi-layer polymer, preferably wherein the thermoplastic polymer coating is a polymer coating system comprising one or more layers comprising thermoplastic resins such as polyesters or polyolefins, acrylic resins, polyamides, polyvinyl chloride, fluorocarbon resins, polycarbonates, styrene type resins, ABS resins, chlorinated polyethers, ionomers, urethane resins and functionalised polymers; and/or copolymers thereof; and or blends thereof.

[0026] According to a second aspect of the invention the blackplate provided with a chromium metal - chromium oxide coating obtained by the process according to the invention has a shiny coating is shiny and shows no stripy appearance. The invention is also embodied in the use of the chromium metal - chromium oxide coated blackplate obtainable by the process according to the invention in a process to produce containers for packaging purposes.

EXAM PLE

[0027] An electrolyte was prepared having a sodium formate concentration of 20 g/l (294 mM), a sodium sulphate concentration of 80 g/l (563 mM) and a pH of 2.6, 2.15 and 2.0, and a chromium concentration of 10 g/l (192 mM). The formate/Cr^{3+} ratio = 1.53. At each of these pH-values the appearance is not stripy, with the better appearance being obtained with the lower pH-values. Stripe free and shiny surfaces were obtained at line speeds of 100 and 200 m/min or higher.

[0028] In addition to the improvement of surface appearance by the reduction in pH there are additional advantages as a result of the lower Cr^{3+} in comparison to the prior art of WO2014202316-A1 (Cr^{3+} = 385 mM, pH 2.6). The higher current efficiency has already been mentioned and shown in Figure 2. In addition, because of the lower concentrations in the electrolyte, the degree of dragout losses will also be reduced. It is also believed that the edge build-up is reduced, and the lower sulphate content of the electrolyte is likely to result in lower sulphate contents in the deposited coating layer, which is beneficial for lacquer adherence.

[0029] The deposition mechanism of the chromium layer from the electrolyte solution according to the invention is assumed to be based on a fast, stepwise deprotonation of the water ligands in the Cr^{3+}-formate complex ion induced by a surface pH increase as a result of hydrogen evolution ($2H^+ + 2e^- \rightarrow H_2(g)$) (See Figure 3 and 4):

$$[Cr(HCOO)(H_2O)_5]^{2+} + OH^- \rightarrow [Cr(HCOO)(OH)(H_2O)_4]^+ + H_2O \qquad \text{(regime I)}$$

$$[Cr(HCOO)(OH)(H_2O)_4]^+ + OH^- \rightarrow Cr(HCOO)(OH)_2(H_2O)_3\downarrow + H_2O \qquad \text{(regime II)}$$

$$Cr(HCOO)(OH)_2(H_2O)_3\downarrow + OH^- \rightarrow [Cr(HCOO)(OH)_3(H_2O)_2]^- + H_2O \qquad \text{(regime III)}$$

[0030] In regime II (See Figure 4), a mixed Cr-metal-carbide-oxide coating is deposited on the steel substrate. In regime I there is no deposition of chromium, and in regime III the amount of deposited chromium drops sharply.

[0031] The current density at which the desired chromium coating weight and composition are obtained, depends on the electrolyte composition, pH, temperature and mass transfer rate (strip speed in case of a strip plating line). In practice, the optimal current density is not a discrete value, but a range of values restricted by a lower and an upper limit. This current density range is called the 'plating window'. Within the plating window, the coating properties fall within certain specifications. From an operational perspective, a large plating window is desired, because this simplifies process control.

[0032] Experiments were performed for investigating the influence of the chromium and formate concentration on the plating window.

TABLE 1: RCE-EXPERIMENTS

electrolyte solution	I		II		III	
	g l^{-1}	M	g l^{-1}	M	g l^{-1}	M
sulphate	127.0	1.322	140.0	1.457	170.0	1.770
TOC	7.8	0.649	7.8	0.649	9.2	0.766
Cr	18.1	0.349	21.2	0.408	24.9	0.479
Fe	0.6	0.011	0.7	0.012	0.6	0.010
Na	49.8	2.164	58.0	2.523	61.1	2.658
$CrOHSO_4$ basic chromium(III)sulphate	57.6	0.349	67.3	0.408	79.0	0.479
HCOONa sodium formate	44.2	0.649	44.2	0.649	52.1	0.766
Na_2SO_4 sodium sulphate	107.6	0.758	133.1	0.937	134.4	0.946

(continued)

electrolyte solution	I		II		III	
	g l^{-1}	M	g l^{-1}	M	g l^{-1}	M
formate/Cr^{3+} molar ratio	1.86		1.59		1.60	
pH	2.8		2.8		2.8	
TOC=Total Organic Carbon						

[0033] For the electrodeposition experiments titanium anodes comprising a catalytic coating or mixed metal oxide of iridium oxide and tantalum oxide are chosen. The rotational speed of the RCE was kept constant at 776 RPM ($\Omega^{0.7}$ = 6.0 $s^{0.7}$). The substrate was a 0.183 mm thick cold rolled blackplate material and the dimensions of the cylinder were 113.3 mm x ø 73 mm. The cylinders were cleaned and activated under the following conditions prior to plating.

TABLE 2: PRETREATMENT OF THE SUBSTRATE

	step 1	step 2
	cleaning	activation
solution composition	50 ml·l^{-1} Chela Clean KC-25H	25 g·l^{-1} H_2SO_4
temperature (°C)	60	25
current density (A·dm^{-2})	+1.5 (anodic)	0 (dip)
Time (s)	60	1.5

[0034] In figure 2 the results of coating trials with these compositions are given.

[0035] In a preferred embodiment an organic coating is provided on one or both sides of the chromium metal - chromium oxide coated blackplate substrate. It was found that organic coatings could be readily applied on to the chromium-chromium oxide coating, which itself acts a passivation layer to protect the electrically conductive substrate. The chromium-chromium oxide coating also exhibited good adhesion the subsequently applied organic coating. The organic coating may be provided as a lacquer or as a thermoplastic polymer coating. Preferably the thermoplastic polymer coating is a polymer coating system that comprises one or more layers of thermoplastic resins such as polyesters or polyolefins, but can also include acrylic resins, polyamides, polyvinyl chloride, fluorocarbon resins, polycarbonates, styrene type resins, ABS resins, chlorinated polyethers, ionomers, urethane resins and functionalised polymers. For clarification:

- Polyester is a polymer composed of dicarboxylic acid and glycol. Examples of suitable dicarboxylic acids include therephthalic acid, isophthalic acid, naphthalene dicarboxylic acid and cyclohexane dicarboxylic acid. Examples of suitable glycols include ethylene glycol, propane diol, butane diol, hexane diol, cyclohexane diol, cyclohexane dimethanol, neopentyl glycol etc. More than two kinds of dicarboxylic acid or glycol may be used together.
- Polyolefins include for example polymers or copolymers of ethylene, propylene, 1-butene, 1-pentene, 1-hexene or 1-octene.
- Acrylic resins include for example polymers or copolymers of acrylic acid, methacrylic acid, acrylic acid ester, methacrylic acid ester or acrylamide.
- Polyamide resins include for example so-called Nylon 6, Nylon 66, Nylon 46, Nylon 610 and Nylon 11.
- Polyvinyl chloride includes homopolymers and copolymers, for example with ethylene or vinyl acetate.
- Fluorocarbon resins include for example tetrafluorinated polyethylene, trifluorinated monochlorinated polyethylene, hexafluorinated ethylene-propylene resin, polyvinyl fluoride and polyvinylidene fluoride.
- Functionalised polymers for instance by maleic anhydride grafting, include for example modified polyethylenes, modified polypropylenes, modified ethylene acrylate copolymers and modified ethylene vinyl acetates.

[0036] Mixtures of two or more resins can be used. Further, the resin may be mixed with anti-oxidant, heat stabiliser, UV absorbent, plasticiser, pigment, nucleating agent, antistatic agent, release agent, anti-blocking agent, etc. The use of such thermoplastic polymer coating systems have shown to provide excellent performance in can-making and use of the can, such as shelf-life.

[0037] The application process of the thermoplastic polymer coating is preferably performed by laminating a polymer film onto the coated blackplate by means of extrusion coating and lamination, wherein a polymer resin is melted and formed into thin hot film, which is coated onto the moving substrate. The coated substrate then usually passes between a set of counter-rotating rolls, which press the coating onto the substrate to ensure complete contact and adhesion. The alternative is film lamination, where a film of the polymer is supplied and coated onto a heated substrate and pressed onto the substrate by and between a set of counter-rotating rolls to ensure complete contact and adhesion.

[0038] The invention will now be explained by means of the following, non-limiting figures.

Figure 1: Schematic process route of starting material for the coating process according to the invention.
Figure 2: Deposition curve as a function of i (A/dm^2) for electrolyte solutions with a different chromium(III)concentration (18.1 g/l = 349 mM, 21.2 g/l = 408 mM, 24.9 g/l = 479 mM).
Figure 3: Schematic principle of the chromium deposition mechanism
Figure 4: Chromium coating weight as a function of current density showing the 3 different deposition regimes.

Claims

1. Method for manufacturing a chromium metal - chromium oxide coated blackplate by electrolytically depositing the chromium metal - chromium oxide coating on blackplate in a continuous high speed plating line operating at a line speed of at least 50 m/min from an electrolyte solution comprising a trivalent chromium compound, wherein the electrolyte solution is free of chloride ions and of a boric acid buffering agent, the electrically conductive substrate acts as a cathode and an anode comprising a catalytic coating of iridium oxide or a mixed metal oxide for reducing or eliminating the oxidation of Cr^{3+}-ions to Cr^{6+}-ions, wherein the electrolyte solution contains at most 250 mM Cr^{3+}-ions, a complexing agent at a

$$\left(\frac{complexing\ agent}{Cr^{3+}}\right)$$

molar ratio of at least 1:1, 0 to 2800 mM of sodium sulphate (Na_2SO_4), a pH of between 1.5 and 3.0 measured at 25 °C, and wherein the plating temperature is between 30 and 70 °C.

2. Method according to claim 1 wherein the complexing agent is formate ($HCOO^-$), preferably added to the electrolyte solution as sodium formate (HCOONa).

3. Method according to claim 1 wherein the Cr^{3+}-ions are provided by a water soluble chromium(III) salt and wherein the water soluble chromium(III) salt preferably is one or more of the following water soluble chromium(III) salts:

   - basic chromium(III)sulphate
   - chromium(III)formate
   - chromium(III)oxalate
   - chromium(III)acetate.

4. Method according to claim 1 or 2 wherein the electrolyte solution contains at most 225 mM of Cr^{3+}-ions, and/or at least 100 mM of Cr^{3+}-ions, preferably at least 125 mM of Cr^{3+}-ions.

5. Method according to any one of the preceding claims wherein the pH of the electrolyte solution is at most 2.8, preferably at most 2.6, more preferably at most 2.2.

6. Method according to any one of the preceding claims wherein the formate/Cr^{3+} molar ratio is at most 2.5:1.

7. Method according to any one of the preceding claims wherein the electrolyte solution contains at least 75 mM and/or at most 600 mM of sodium formate.

8. Method according to any one of the preceding claims wherein the electrolyte solution contains at least 210 mM and/or at most 845 mM of sodium sulphate.

9. Method according to any one of the preceding claims wherein the plating temperature is at least 40 °C, preferably

at least 50 °C, more preferably at least 55 °C.

10. Method according to any one of the preceding claims wherein the line speed of the plating line is at least 100 m/min.

11. Method according to any one of the preceding claims wherein the coated blackplate is further coated on one or both sides by a film lamination step or a direct extrusion step, with an organic coating consisting of a thermoplastic single layer, or a thermoplastic multi-layer polymer.

12. Method according to claim 11 preferably wherein the thermoplastic polymer coating is a polymer coating system comprising one or more layers comprising thermoplastic resins such as polyesters or polyolefins, acrylic resins, polyamides, polyvinyl chloride, fluorocarbon resins, polycarbonates, styrene type resins, ABS resins, chlorinated polyethers, ionomers, urethane resins and functionalised polymers; and/or copolymers thereof; and or blends thereof.

13. Method according to claim 11 wherein the thermoplastic polymer coating on the one or both sides of the coated blackplate is a multi-layer coating system, said coating system comprising at least an adhesion layer for adhering to the coated blackplate, a surface layer and a bulk layer between the adhesion layer and the surface layer, wherein the layers of the multi-layer coating system comprise or consist of polyesters, such as polyethylene terephthalate, IPA-modified polyethylene terephthalate, CHDM-modified polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, or copolymers or blends thereof.

14. Blackplate provided with a chromium metal - chromium oxide coating obtainable by the process according to any one of claims 1 to 10, wherein the surface of the coating is shiny and shows no stripy appearance.

15. Use of the chromium metal - chromium oxide coated blackplate obtainable by the process according to any one of claims 1 to 13, in a process to produce containers for packaging purposes.

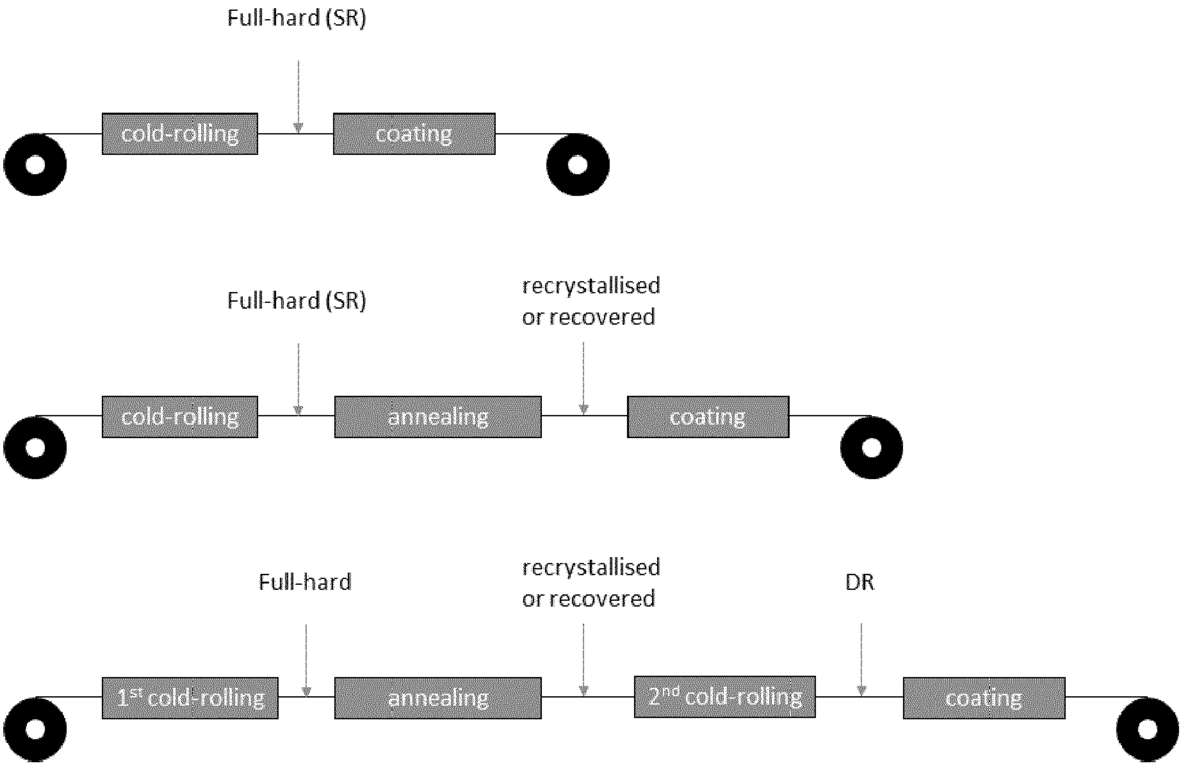


FIGURE 1

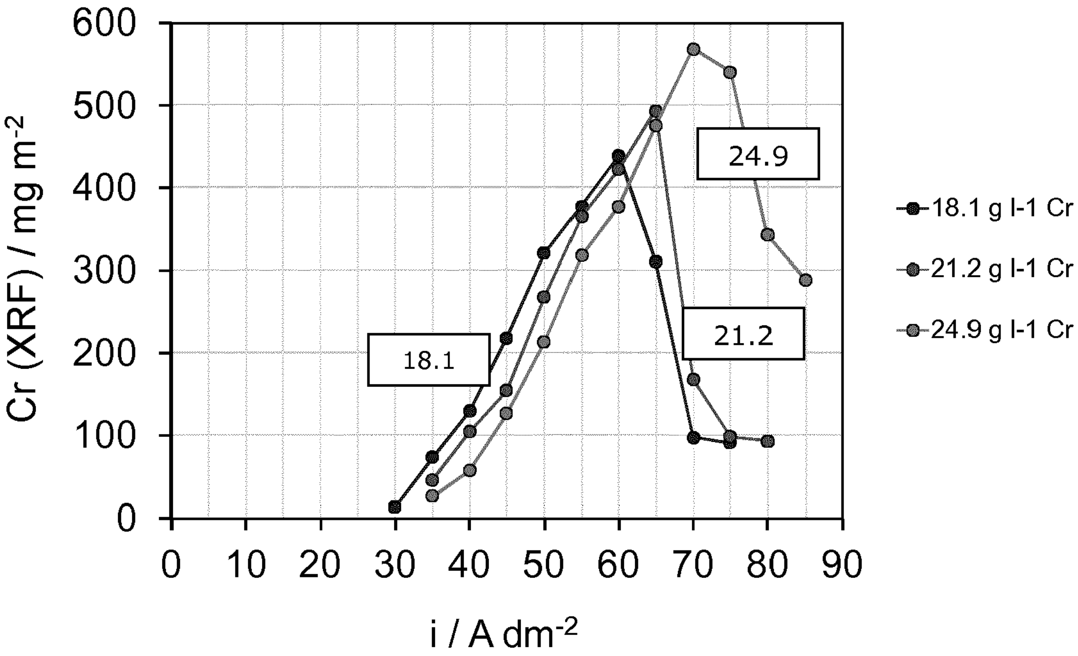
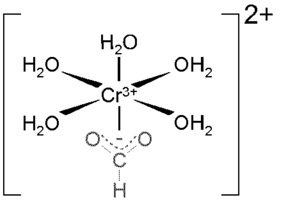
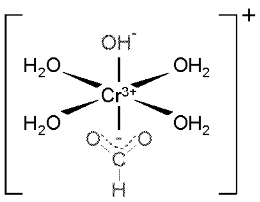
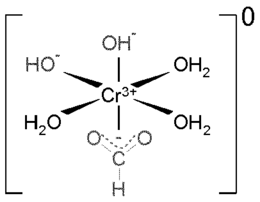
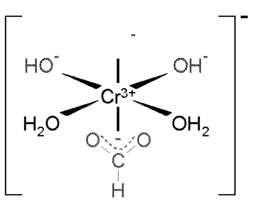


FIGURE 2

equilibrium pH < 2.8	regime I	regime II	regime III
			

Ref. Electrochim. Acta, **213** (2016) 194 – 200.

FIGURE 3

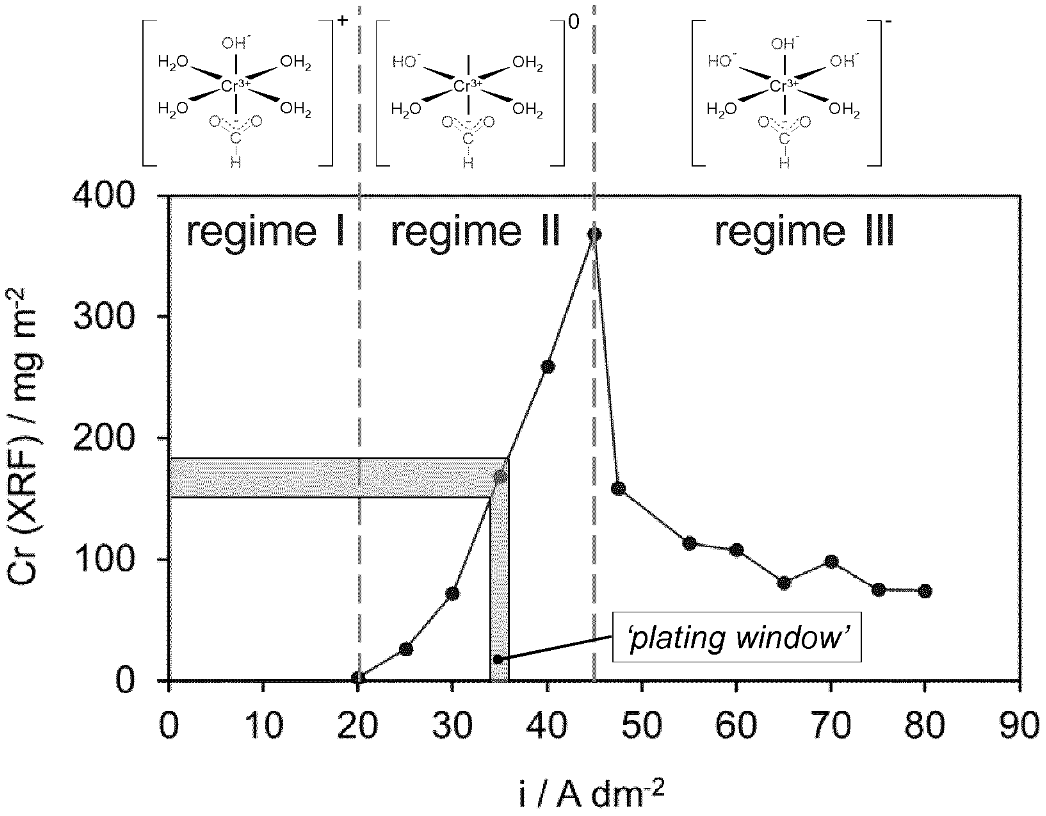


FIGURE 4

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EUROPEAN SEARCH REPORT

Application Number
EP 17 16 2054

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2015/177314 A1 (TATA STEEL IJMUIDEN BV [NL]) 26 November 2015 (2015-11-26)	1-5, 7-10,14, 15	INV. C25D3/06 C25D5/48 C25D9/08 C25D9/10
Y	* paragraph [0031]; claims 1, 10 * * paragraph [0038] * * paragraph [0042] * * paragraph [0052] - paragraph [0056] * -----	6,11-13	
A	JP 2016 060918 A (JCU CORP) 25 April 2016 (2016-04-25) * paragraph [0001] * * paragraph [0011] * * paragraph [0021] * * paragraph [0026] * -----	1-15	
Y,D	WO 2014/202316 A1 (TATA STEEL IJMUIDEN BV [NL]) 24 December 2014 (2014-12-24) * page 8, line 12 - page 9, line 15; claim 11 * -----	11-13	
Y	US 4 167 460 A (TOMASZEWSKI THADDEUS W) 11 September 1979 (1979-09-11) * claim 4 * -----	6	TECHNICAL FIELDS SEARCHED (IPC) C25D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	20 September 2017	Telias, Gabriela

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 17 16 2054

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015177314 A1	26-11-2015	CA 2947794 A1	26-11-2015
		CN 106414806 A	15-02-2017
		EP 3146092 A1	29-03-2017
		JP 2017519103 A	13-07-2017
		KR 20170007268 A	18-01-2017
		US 2017081773 A1	23-03-2017
		WO 2015177314 A1	26-11-2015
JP 2016060918 A	25-04-2016	NONE	
WO 2014202316 A1	24-12-2014	CA 2915523 A1	24-12-2014
		CN 105473767 A	06-04-2016
		DK 3011080 T3	21-08-2017
		EP 3011080 A1	27-04-2016
		JP 2016528378 A	15-09-2016
		KR 20160024909 A	07-03-2016
		RU 2016101343 A	25-07-2017
		US 2016138178 A1	19-05-2016
		WO 2014202316 A1	24-12-2014
US 4167460 A	11-09-1979	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2014202316 A1 **[0005] [0012] [0028]**