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(54) METHOD OF PRODUCING AN ELECTROLYTE FOR ELECTRODEPOSITION OF A CHROMIUM-CHROMIUM OXIDE LAYER

(57) Method of producing a plating electrolyte free of sulphite for electrodepositing a chromium metal - chromium oxide coating layer on a steel substrate in a continuous high speed plating line operating at a line speed of at least 60 m/min, wherein the plating electrolyte comprises a trivalent chromium compound and wherein the plating electrolyte is free of chloride ions, free of Cr^{6+}-ions, free of boric acid.

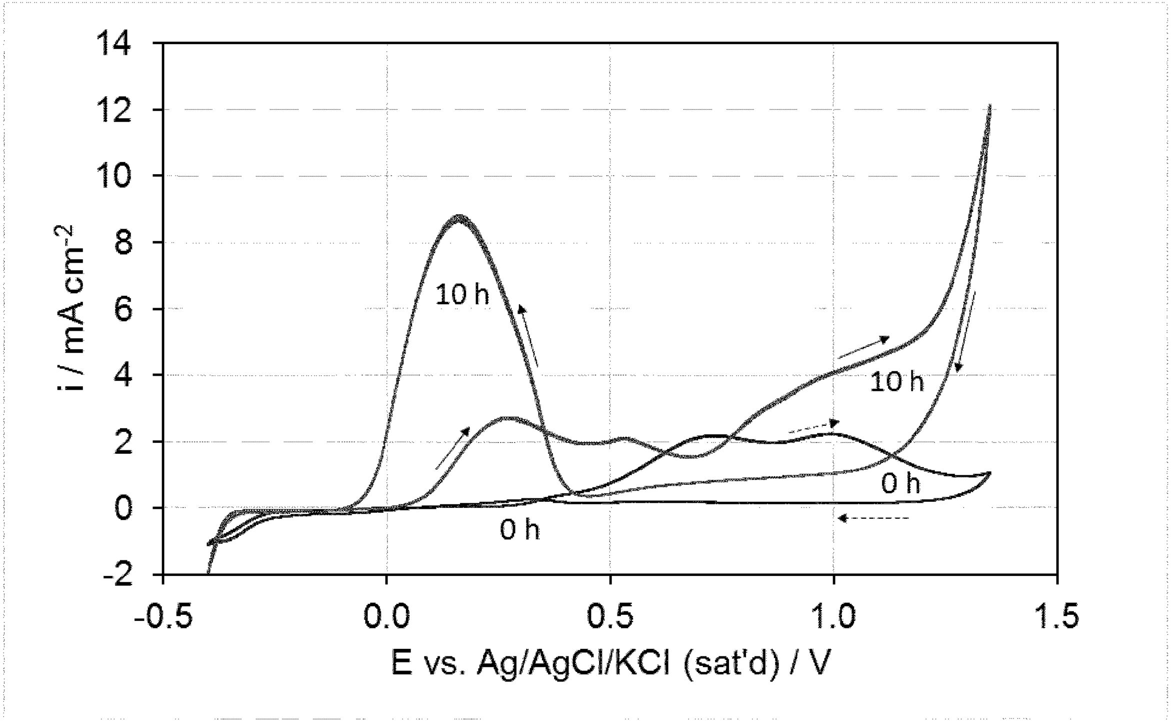

FIGURE 5

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Description

[0001] This invention relates to a method of producing an electrolyte for electrodeposition of a chromium-chromium oxide layer on a metal strip.

[0002] Recently, much attention has been given to the development of REACH compliant alternatives for the hexavalent chromium electrolytes still used for the production of steels for the packaging industry, such as ECCS. ECCS is an acronym for Electrolytic Chromium Coated Steel. ECCS is also often called Tin Free Steel (TFS), because this material was originally developed as a lower cost alternative for tinplate due to the high tin prices at the time. This material consists of a thin gauge (0.10 - 0.49 mm) low-carbon steel substrate with a very thin coating comprising a base layer of chromium metal (50 - 150 mg/m^2) and a top layer of chromium oxide (7 - 35 mg/m^2). This material is particularly suitable for use in the packaging industry. ECCS is typically used in the production of DRD two-piece cans and components that do not have to be welded, such as ends, lids, crown corks, twist-off caps and aerosol bottoms and tops. ECCS excels in adhesion to organic coatings. There are also many examples of 'non-packaging' applications of ECCS, like automotive components (oil filters, cylinder head gaskets), building trade (space bars for double glazing, light reflectors) and house ware (cake tins, gas canister components).

[0003] Traditional chromium electrolytes contain hexavalent chromium, which is usually added to the electrolyte as chromium trioxide (CrO_3). Hexavalent chromium is nowadays considered a hazardous substance that is potentially harmful to the environment and constitutes a risk in terms of worker safety. To comply with occupational safety and health regulations, the toxicity of hexavalent chromium requires an expensive exhaust system to capture any aerosols being released during electrolysis and also a complex waste water treatment of the effluents. The harmfulness of hexavalent chromium (Cr(VI), Cr^{6+}) is attributed to its high oxidising potential and its easy permeation of biological membranes. In contrast, trivalent chromium (Cr(III), Cr^{3+}) is not known to be harmful to body tissue. In fact, it is an important component of a balanced human and animal diet and a deficiency is detrimental to the glucose and lipid metabolism in mammals. Therefore, trivalent chromium plating is considered a benign technology to replace hexavalent chromium plating.

[0004] In the development of an electrolyte based on trivalent chromium such as in WO20141202316 a problem was encountered in that sulphite pollution of the electrolyte prevented the deposition of the desired chromium-chromium oxide layer on the metallic substrate.

[0005] It is the object of this invention to provide an improved method for preparing a sulphite free electrolyte for electroplating an uncoated steel strip with a Cr-CrOx plating layer from a trivalent Cr-electrolyte.

[0006] The object of this invention is reached by a method of producing a plating electrolyte for electrodepositing a chromium metal - chromium oxide coating layer on a steel substrate in a continuous high speed plating line operating at a line speed of at least 60 m/min, wherein the plating electrolyte comprises a trivalent chromium compound and wherein the plating electrolyte is free of chloride ions, free of Cr6+-ions and free of boric acid, wherein the plating electrolyte contains:

- basic chromium(III) sulphate and optionally chromium(III) formate,
- one or more of formic acid, sodium formate and potassium formate as complexing agent,
- one or more of sulphuric acid, sodium sulphate and potassium sulphate,
- optionally sulphuric acid or sodium hydroxide to adjust the pH of the electrolyte to a value of between 1.0 and 3.0 measured at 25 °C,

to obtain a plating electrolyte which is free from sulphite ions and wherein the plating electrolyte contains at most 500 mM Cr^{3+}-ions, complexing agent at a

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

molar ratio of at least 1:1, 0 to 2800 mM of sulphate (SO_4^{2-}).

[0007] The inventors made the observation that a fresh electrolyte solution produced in accordance with this method on the basis of commercially available basic chromium(III) sulphate concentrate contained sulphite ions. These sulphite ions were found to adversely affect the plating quality of the chromium-chromium oxide plating layer deposited on a steel strip. The desired chromium coating weight could not be deposited with an acceptable appearance. After a thorough investigation of all relevant parameters the investors found that the presence of the sulphite ions was the source of the problem.

[0008] Consequently the identification of the problem also presented the solution in that the fresh electrolyte solution may not contain sulphite ions.

[0009] The final plating electrolyte therefore contains:

- basic chromium(III) sulphate and optionally chromium(III) formate,
- as complexing agent one or more of formic acid, sodium formate, potassium formate, one or more of sodium sulphate and potassium sulphate,
- and optionally sulphuric acid or sodium hydroxide to adjust the pH of the electrolyte to a value of between 1.0 and 3.0 measured at 25 °C,

and no sulphite ions, no chloride ions, no Cr^{6+}-ions and no boric acid

[0010] One obvious way to provide an electrolyte solution without sulphite ions is to prevent the addition of sulphite ions to the solution. However, when using basic chromium(III)sulphate as the source for the Cr^{3+}-ions this appeared to be troublesome. The inventors were able to identify that the source of the sulphite pollution in the plating electrolyte was the basic chromium(III) sulphate concentrate that is used for the preparation of the plating electrolyte.

[0011] Basic chromium(III) sulphate (CAS # 12336-95-7), also known as an important ingredient for the tanning of leather, can be manufactured by reducing Cr(VI) to Cr(III) by the addition of an excess of sulphur dioxide:

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \leftrightarrows (CrOHSO_4)_2 \cdot Na_2SO_4 \qquad (1)$$

Any excess SO_2 will result in the following reaction:

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad (2)$$

[0012] The sulphurous acid (H_2SO_3) will end up as a contaminant in the final basic chromium(III) sulphate and is identified as the source of the sulphite-ions in the electrolyte solution. In the aqueous solution the sulphurous acid will dissociate in SO_3^{2-} and H^+ (or H_3O^+). This reaction can be reversed by making the concentrated solution containing the dissolved basic chromium(III) sulphate or basic chromium(III) sulphate acidic:

$$SO_3^{2-} + 2H^+ \leftrightarrows SO_2\uparrow + H_2O \qquad (2a)$$

The term concentrated solution can be any concentration between a substantially undiluted concentrated solution and the final electrolyte solution suitable for disposal in the plating cells. The advantage of using a concentrated solution is that the amount of acid needed to drive out the SO_2 is smaller than when using a fully diluted solution, because the SO_2 is driven out by the pH reaching the value needed to shift the equilibrium reaction (2a) to the right. So the degree of concentration of the concentrated solution is relatively unimportant and more or less cost driven: the higher the concentration, the lower the amount of acid needed to drive out the SO_2. After all SO_2 has been driven out from the (concentrated) solution sodium hydroxide or potassium hydroxide is added to the acid concentrated solution to reduce the acidity. Also formate-ions as complexing agent are added by adding a suitable amount of one or more of formic acid, sodium formate, potassium formate and chromium(III) formate to the concentrated solution to obtain the desired molar ratio of (complexing agent/Cr^{3+}). Water is added to the solution until an electrolyte solution with the desired concentration of Cr(III) of at most at most 500 mM Cr^{3+}-ions is obtained, and finally sulphuric acid or sodium hydroxide or potassium hydroxide can be added to the electrolyte solution to adjust the pH to the desired value to obtain the final plating solution (see Figure 1 and the explanation thereof below).

[0013] Surprisingly, it was found that sulphite is not oxidised to sulphate at the anode. The sulphite is therefore not present as a free ion, but is likely to be in the form of a Cr(III)-complex. The presence of a chromium dimer species with the formulation $[Cr_2(H_2O)_8(S_2O_6)_2]^3$ in SO_2 reduced liquors is reported in literature (e.g. in B. Chandrasekaran, J. Raghava Rao, K.J. Sreeram, B.U. Nair, T. Ramasami, 'Chrome Tanning: State-of-Art on the Material Composition and Characterization', J. Sci. Ind. Res., 58 (1999) (pp 1 - 10).

[0014] The plating electrolyte is made free from sulphite ions by preparing the plating electrolyte in accordance with the following steps:

1. dissolving basic chromium(III) sulphate or basic chromium(III) sulphate concentrate in an initial amount of water to produce a concentrated solution;
2. adding sulphuric acid to the concentrated solution to make an acid concentrated solution and remove sulphite from the solution according to:

    a.

$$SO_3^{2-} + 2H^+ \leftrightarrows SO_2\uparrow + H_2O \qquad (2a)$$

3. allowing the SO_2 to escape from the acid concentrated solution;
4. adding sodium hydroxide or potassium hydroxide to the acid concentrated solution;
5. adding formate-ions as complexing agent by adding a suitable amount of one or more of

    i. formic acid
    ii. chromium(III) formate
    iii. sodium formate
    iv. potassium formate

to the concentrated solution to obtain the desired molar ratio;
6. adding water to the concentrated solution until a plating electrolyte with the desired concentration of Cr(III) of at most at most 500 mM Cr^{3+}-ions is obtained;
7. adding sulphuric acid or sodium hydroxide or potassium hydroxide to the plating electrolyte to adjust the pH to the desired value.

[0015] Whether or not the final plating solution still contains sulphite can be detected by means of cyclic voltammetry (CV). The addition of chromium(III) formate to the solution is not believed to introduce sulphite into the solution, but even if it did, then the sulphite would be removable in the same way as the sulphite introduced along with the basic chromium(III) sulphate.

[0016] In a preferable embodiment the electrolyte solution contains at most 250 mM of Cr^{3+}-ions, more preferably 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 in preventing a stripy appearance of the deposited surface is usually associated with a certain inhomogeneity in the electroplating process. The inventors found that by increasing the chromium(III) content in comparison to the content in the state of the art (WO2014202316 discloses a Cr^{3+} electrolyte using 120 g/l (= 385 mM) basic chromium(III)sulphate), 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 from an electrolyte according to the method of the invention.

[0017] In an embodiment the pH of the electrolyte solution is at least 1.5, and/or 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.

[0018] 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.

[0019] 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.

[0020] In an embodiment the electrolyte solution contains at least 210 mM and/or at most 845 mM of sodium sulphate. In an embodiment only sodium hydroxide is used in the plating electrolyte, and no potassium hydroxide. In an embodiment sodium formate and/or formic acid and/or chromium(III) formate is used as a source of formate-ions in the plating electrolyte, and no potassium formate is used. In these embodiments the amount of potassium in the plating solution is minimised and the amount of sodium is maximised, which is beneficial for the plating operation.

[0021] In a preferable embodiment the electrolyte solution is made free from sulphite ions by disposing the final electrolyte solution in one, more or all of the plating cells of the continuous high speed plating line and leading an electrically conductive substrate acting as the cathode through the plating line wherein a current is applied to the strip as cathode and entering the plating cell or cells and an insoluble anode which current is insufficient to deposit a plating layer from the trivalent Cr-electrolyte, but which is sufficient to reduce the sulphite ions to sulphide, and thereby removing the sulphite-ions from the electrolyte solution, and wherein the sulphide escapes from the electrolyte solution in the form of H_2S. Preferably the anode(s) comprise(s) a catalytic coating of iridium oxide or a mixed metal oxide. In a preferred embodiment the mixed metal oxide comprises oxides of iridium and tantalum.

[0022] This catalytic coating reduces or fully eliminates the oxidation of Cr^{3+}-ions to the undesired and potentially harmful Cr^{6+}-ions. The electrically conductive substrate can be cold-rolled steel substrates which can be used once, or over and over again, e.g. stainless steel strips which are unaffected by passing them through the process, or rejected coils which may be re-used or scrapped afterwards. The removal of the sulphite in this process is a diffusion based process, and is time-consuming. It may take several hours (even up to 10-15 hours) to drive out all sulphite from a fresh plating electrolyte. This process is called dummy plating, because a strip is processed through the plating line, but no deposit is made on the strip. To achieve a metal deposit an increased current (current density) is required. The only result of the dummy plating is that the sulphite is removed from the plating electrolyte. By means of CV the plating electrolyte can be tested for the presence of sulphite.

[0023] Once cleaned, the solution stays free from sulphite as long as no new sulphite is introduced by adding new basic chromium(III) sulphate. When basic chromium (III)sulphate is added to replenish the chromium plated from the solution, then the amount of sulphite that is being introduced is relatively small and does not adversely affect the quality of the plating layer to any significant degree. Moreover, any added sulphite as a result of replenishment is removed from the solution during normal plating similar to the dummy plating process but in this case while simultaneously depositing an acceptable coating layer. Depositing an acceptable coating layer is not possible with a completely fresh solution, because then the sulphite concentration is much higher.

[0024] In another embodiment of the invention a method is provided wherein the plating electrolyte is made free from sulphite ions by

- disposing the plating electrolyte in one, more or all of the plating cells of the continuous high speed plating line;
- leading the steel substrate acting as the cathode through the plating line wherein a current is applied between an anode and the substrate entering the plating cell or cells which current is insufficient to deposit a plating layer from the trivalent Cr-electrolyte, but which is sufficient to reduce the sulphite ions to sulphide at the cathode, and thereby removing the sulphite-ions from the electrolyte solution, and wherein the sulphide escapes from the electrolyte solution in the form of H_2S.

[0025] In still another embodiment a method is provided wherein the plating electrolyte is disposed in a holding vessel or container (not being a plating cell of a continuous high speed plating line) wherein a current is applied between a cathode and an anode placed in the plating electrolyte which current is insufficient to deposit a plating layer from the plating electrolyte onto the cathode, but which is sufficient to reduce the sulphite ions to sulphide at the cathode, wherein the sulphide escapes from the electrolyte solution in the form of H_2S, thereby removing the sulphite-ions from the plating electrolyte to produce a clean plating electrolyte for use in the plating cells of a continuous high speed plating line.

[0026] The method according to the invention can be identified as dummy plating, because an electrically conductive substrate is led through the plating cells and electrolyte solution under current, but without actual plating taking place. The only result of the dummy plating is that the sulphite is removed from the plating solution. It is possible to use a dummy steel strip for this process which can be used over and over again, or a commercial strip that is led through the plating cell and electrolyte more than once, the last time at a current sufficient to deposit a plating layer from the trivalent Cr-electrolyte.

[0027] By performing the dummy plating in a container or holding vessel the plating line can be used for plating, and no production time is consumed by first having to remove the sulphite from the plating electrolyte. The sulphide-free electrolyte can be stored in the container or holding vessel until it is needed to replenish the electrolyte in the plating cell(s).

[0028] The invention is also embodied in a method of producing a chromium-chromium oxide coating on a steel strip, wherein the coated steel strip is preferably used for the production of cans or containers, lids or other packaging applications. The coated steel strip is particularly suitable for further providing with a polymer coating layer or polymer coating system comprising more than one polymer layer. The chromium-chromium oxide coating may also contain chromium carbide, wherein the carbon from the carbide is believed to originate from the formate ions. The coating may also comprise sulphate.

[0029] As long as the steel strip is suitable for packaging applications the invention is not limited to the use of any specific composition of steel substrate.

[0030] Commercial strip is preferably selected from:

o cold-rolled full-hard blackplate, single or double reduced;
o cold-rolled and recrystallisation annealed blackplate;
o cold-rolled and recovery annealed blackplate,
o tinplate, as deposited or flow-melted;
o tinplate, diffusion annealed with an iron-tin alloy consisting of at least 80% of FeSn (50 at.% iron and 50 at.% tin);

[0031] The invention is also embodied in a method wherein the coated steel substrate is further coated on 1 or 2 sides by film lamination or direct extrusion, with an organic coating consisting of a thermoplastic single layer or 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.

[0032] The invention is also embodied in a method wherein the coated blackplate 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.

[0033] Figure 1 shows the sequence of events in accordance with claim 2.

[0034] In a CV-experiment, the working electrode potential is ramped linearly versus time and the current response is measured (See Figure 2). 10 cycles were programmed between the onset of the Oxygen Evolution Reaction (OER) on the anodic side (Upper Vertex Potential) and the onset of the Hydrogen Evolution Reaction (HER) on the cathodic side. A scan rate of 100 mV/s was chosen, revealing all typical features (peaks) within a practical time for completing 10 cycles (ca. 6 min). In most cases, a few cycles are required for arriving at a stationary condition. In all following figures, the current density vs. potential of the last 5 cycles is plotted, which are nearly identical. The working electrode was a Pt rotating disk electrode (∅ 5 mm) at a rotation rate of 9 s^{-1}. The counter electrode is a fine meshed cylindrical gauze (∅ 30 mm). The reference electrode is a saturated calomel electrode (SCE) or a saturated Ag/AgCl/KCl electrode. The electrolyte temperature was 50 °C and the plating electrolyte had the following basic composition:

Table 1: Electrolyte compositions.

electrolyte	Na_2SO_4 mM	HCOONa mM	$CrOHSO_4$ mM	free formate mM	pH* @ 25 °C
reference electrolyte	900	200	0	200	2.8
plating electrolyte	900	600	400	200	2.8
*The pH was adjusted with sulphuric acid or sodium hydroxide if needed.					

[0035] The typical CV for the reference electrolyte is given in Figure 3. In particular the occurrence of the so-called surface explosion in the reverse negative going sweep is striking, where a combination of advantageous conditions for strong CO_2 formation exist, i.e.:

- A high overpotential for oxidation of formate;
- The availability of metallic Pt;
- The absence of CO poisoning.

[0036] The surface explosion is important for good plating behaviour and the absence of the surface explosion means that bad plating behaviour and bad plating quality is to be expected.

[0037] In Figure 4 the subsequent CV-results of plating electrolyte subjected to dummy plating is presented. The fresh plating electrolyte was tested after 0 hours and then after 1, 3, 5, 6, 8 and 10 hours of dummy plating. Only a part of the CV curve is presented here for clarity. Figure 4 shows the gradual occurrence of the surface explosion with prolonged dummy plating time, and the stabilisation after 10 hours, indicative of the absence of any further sulphite in the plating electrolyte. The fact that the surface explosion re-occurs means that the presence of Cr^{3+} has no effect on the surface explosion peak, and that sulphite is the cause of the suppression of the surface explosion.

[0038] Figure 5 gives a clearer picture of the CV of the fresh plating electrolyte and the electrolyte after 10 hours of dummy plating. This figure gives the entire CV-curve of which only a part was presented in Figure 4.

[0039] Proof that the change in CV is the result of the removal of sulphite as a result of the dummy plating is provided by the smell of H_2S during the dummy plating and the vanishing surface explosion upon addition of Na_2SO_3 to the "cleaned" plating electrolyte. When adding 500 mg/l of Na_2SO_3 the CV is back at the level of the fresh plating electrolyte, suggesting that the fresh plating electrolyte contained about 500 mg/l of sulphite (see Figure 6, showing the surface explosion peak when determining the CV of a cleaned plating electrolyte (i.e. after 10 h of dummy plating), and after the addition of 50, 100, 500, 1000 and 2000 mg/l of Na_2SO_3 respectively. The addition of 500, 1000 or 2000 more or less generates the same curve and the surface explosion peak is absent in all three cases. When adding 50 or 100 mg/l the height of the surface explosion peak decreases, proving that increasing sulphite contamination of the electrolyte causes the absence of the surface explosion peak, and therefore causes the bad plating performance in terms of chromium coating weight and appearance of the chromium layer. The method according to the invention effectively overcomes the sulphite contamination of the electrolyte.

[0040] It has become clear that by means of CV the presence of sulphite can be easily determined and CV is therefore a useful tool in determining the readiness of the plating electrolyte for starting the plating process.

Claims

1. Method of producing a plating electrolyte which is free from sulphite ions for electrodepositing a chromium metal - chromium oxide coating layer on a steel substrate in a continuous high speed plating line operating at a line speed of at least 60 m/min, wherein the plating electrolyte is free of chloride ions, free of Cr^{6+}-ions and free of boric acid and contains:

   - basic chromium(III) sulphate and optionally chromium(III) formate,
   - as complexing agent: one or more of formic acid, sodium formate, potassium formate,
   - one or more of sulphuric acid, sodium sulphate, potassium sulphate,
   - optionally sulphuric acid or sodium hydroxide to adjust the pH of the electrolyte to a value of between 1.0 and 3.0 measured at 25 °C,

   and wherein the plating electrolyte contains at most 500 mM Cr^{3+}-ions, complexing agent at a

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

   molar ratio of at least 1:1, 0 to 2800 mM of sulphate (SO_4^{2-}), wherein the sulphite is removed from the plating electrolyte by converting the sulphite into sulphur dioxide (g) or into hydrogen sulphide (g).

2. Method according to claim 1 wherein the plating electrolyte is made free from sulphite ions by preparing the plating electrolyte in accordance with the following steps:

   - dissolving basic chromium(III) sulphate or basic chromium(III) sulphate concentrate in an initial amount of water to produce a concentrated solution;
   - adding sulphuric acid to the concentrated solution to make an acid concentrated solution and remove sulphite from the solution according to:

   $$SO_3^{2-} + 2H^+ \leftrightarrows SO_2\uparrow + H_2O \qquad (2a)$$

   - allowing the SO_2 to escape from the acid concentrated solution;
   - adding sodium hydroxide or potassium hydroxide to the acid concentrated solution;
   - adding formate-ions as complexing agent by adding a suitable amount of one or more of

     i. formic acid
     ii. chromium(III) formate
     iii. sodium formate
     iv. potassium formate

   to the concentrated solution to obtain the desired molar ratio;

   - adding water to the concentrated solution until a plating electrolyte with the desired concentration of Cr(III) of at most at most 500 mM Cr^{3+}-ions is obtained;
   - adding sulphuric acid or sodium hydroxide or potassium hydroxide to the plating electrolyte to adjust the pH to the desired value.

3. Method according to claim 1, wherein the plating electrolyte is made free from sulphite ions by:

   - disposing the plating electrolyte in one, more or all of the plating cells of the continuous high speed plating line;
   - leading the steel substrate acting as the cathode through the plating line wherein a current is applied between an anode and the substrate entering the plating cell or cells which current is insufficient to deposit a plating

layer from the trivalent Cr-electrolyte, but which is sufficient to reduce the sulphite ions to sulphide, and thereby removing the sulphite-ions from the electrolyte solution, and wherein the sulphide escapes from the electrolyte solution in the form of H_2S

or by

- disposing the plating electrolyte is disposed in a container wherein a current is applied between a cathode and an anode which current is insufficient to deposit a plating layer from the plating electrolyte, but which is sufficient to reduce the sulphite ions to sulphide, wherein the sulphide escapes from the electrolyte solution in the form of H_2S, thereby removing the sulphite-ions from the plating electrolyte to produce a clean plating electrolyte for use in the plating cells of a continuous high speed plating line.

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

5. Method according to any one of the preceding claims wherein only sodium hydroxide is used, and no potassium hydroxide.

6. Method according to any one of the preceding claims wherein only sodium formate and/or formic acid and/or chromium(III) formate is used as a source of formate-ions, and no potassium formate.

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

8. Method according to any one of the preceding claims wherein the plating electrolyte contains at most 250 mM Cr^{3+}-ions.

9. Method according to any one of the preceding claims wherein the plating electrolyte 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.

10. Method according to any one of the preceding claims wherein the plating electrolyte contains at least 75 mM and/or at most 600 mM of formate-ions.

11. Method according to any one of the preceding claims wherein the plating electrolyte contains at least 210 mM and/or at most 845 mM of sulphate-ions.

12. Use of the electrolyte solution produced according to any one of claims 1 to 11 to produce a steel substrate coated with a plating layer comprising chromium metal, chromium carbide and chromium oxide and optionally also comprising chromium sulphate

13. Use according to claim 12 wherein the steel substrate is selected from:

- cold-rolled full-hard blackplate, single or double reduced;
- cold-rolled and recrystallisation annealed blackplate;
- cold-rolled and recovery annealed blackplate,
- tinplate, as deposited or flow-melted;
- tinplate, diffusion annealed with an iron-tin alloy consisting of at least 80% of FeSn (50 at.% iron and 50 at.% tin);

14. Use according to claim 13 wherein the steel substrate 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.

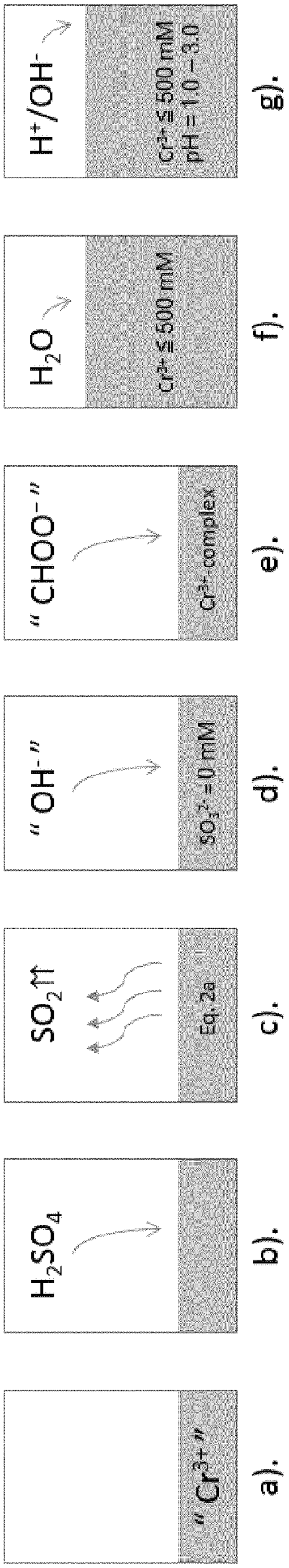
" Cr3+ "
a).
H2SO4
b).
SO2↑↑
Eq. 2a
c).
" OH- "
SO3 2- = 0 mM
d).
" CHOO- "
Cr3+-complex
e).
H2O
Cr3+ ≦ 500 mM
f).
H+/OH-
Cr3+ ≦ 500 mM
pH = 1.0 – 3.0
g).

FIGURE 1

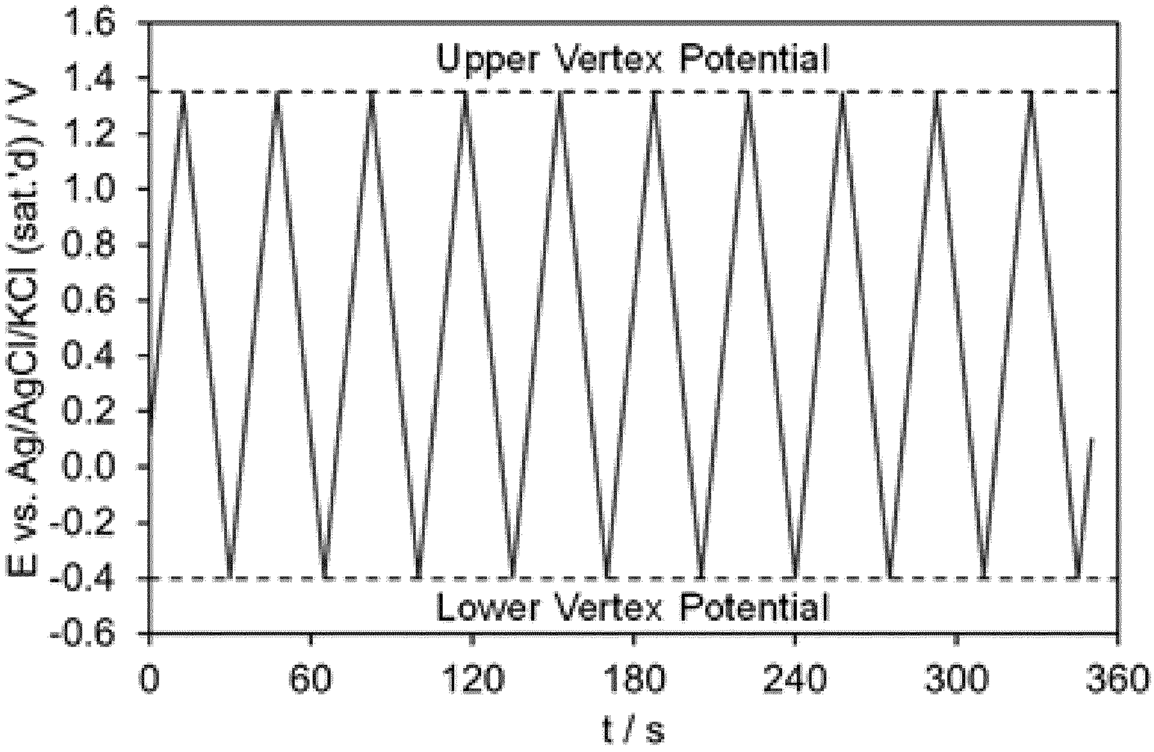

FIGURE 2

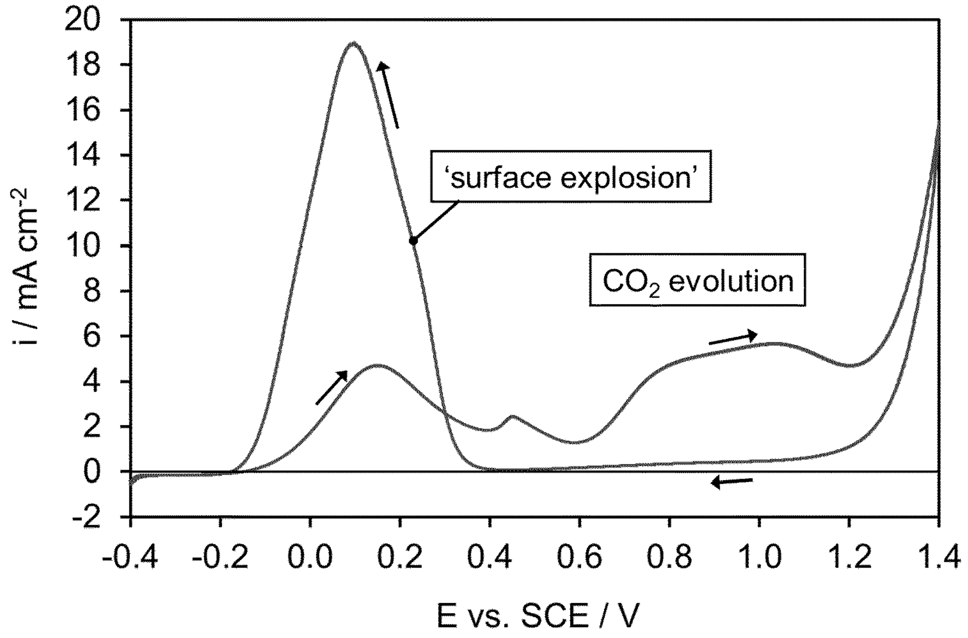

FIGURE 3

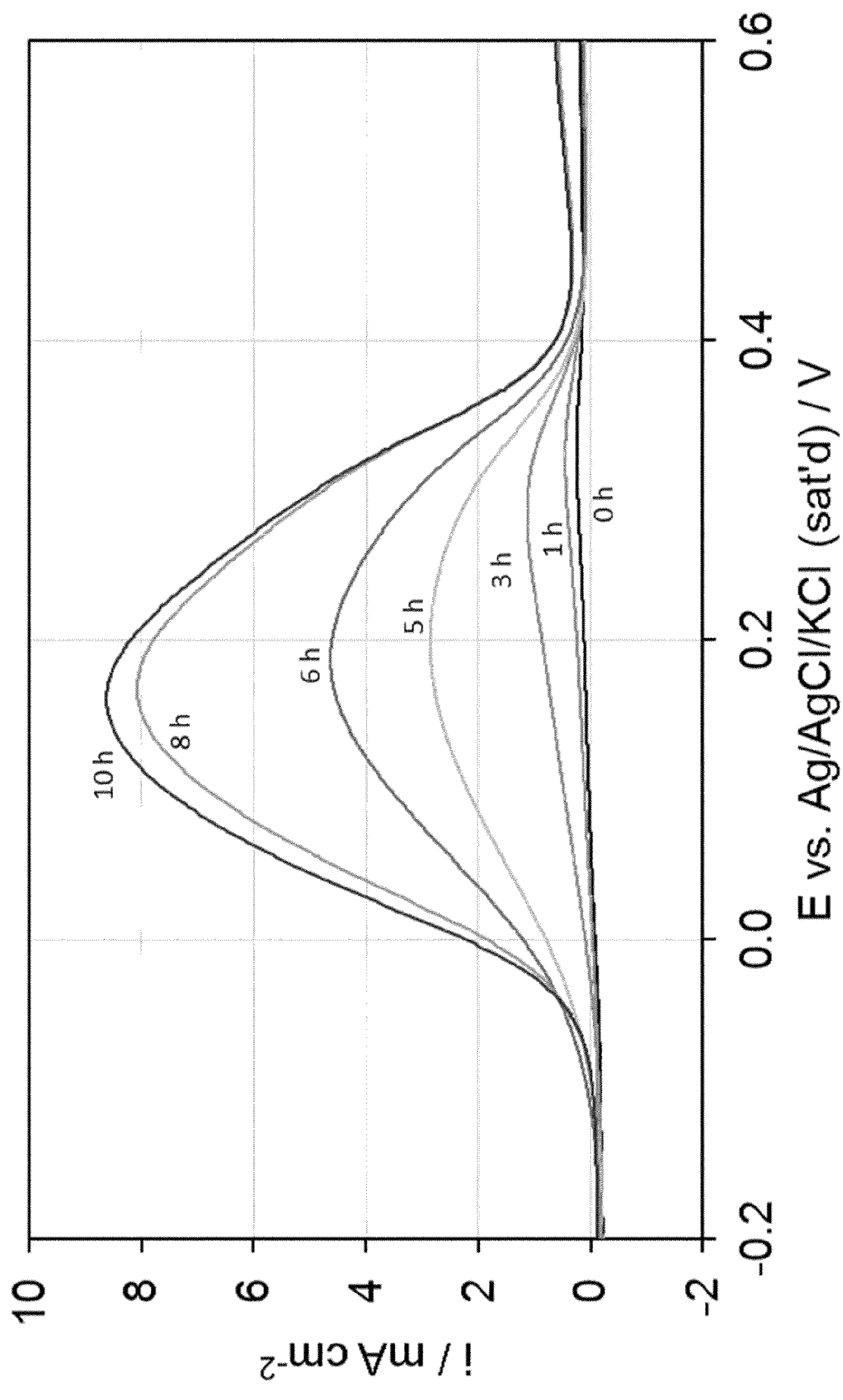
i / mA cm^{-2}
10
8
6
4
2
0
-2
-0.2
0.0
0.2
0.4
0.6
E vs. Ag/AgCl/KCl (sat'd) / V
10 h
8 h
6 h
5 h
3 h
1 h
0 h

FIGURE 4

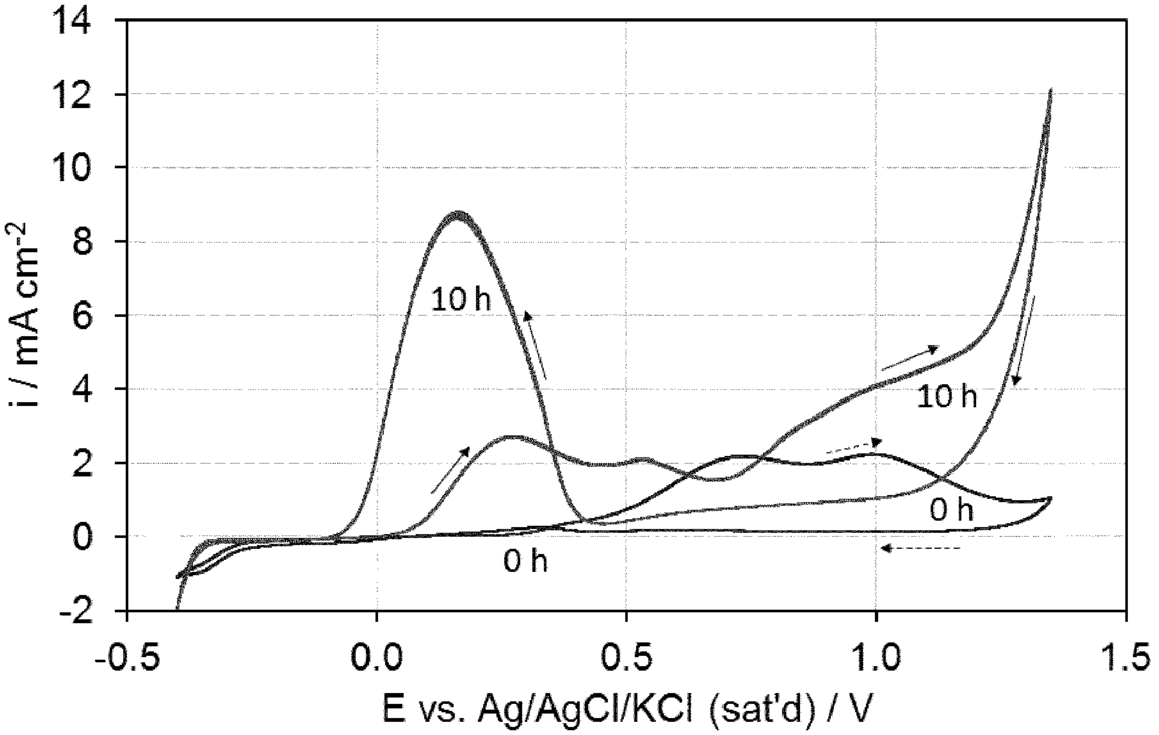
14
12
10
8
6
4
2
0
-2
i / mA cm^{-2}
-0.5
0.0
0.5
1.0
1.5
E vs. Ag/AgCl/KCl (sat'd) / V
10 h
10 h
0 h
0 h

FIGURE 5

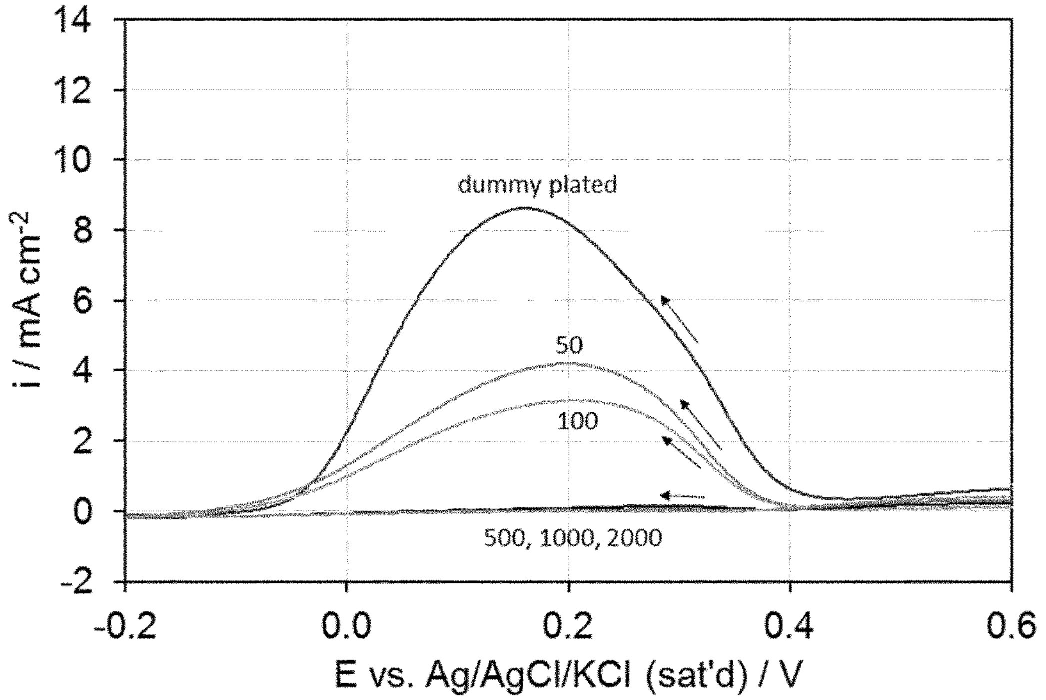
14
12
10
8
6
4
2
0
-2
i / mA cm^{-2}
dummy plated
50
100
500, 1000, 2000
-0.2
0.0
0.2
0.4
0.6
E vs. Ag/AgCl/KCl (sat'd) / V

FIGURE 6

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EUROPEAN SEARCH REPORT

Application Number
EP 18 18 2791

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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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	28 September 2018	Telias, Gabriela

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X : particularly relevant if taken alone
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