(19) Europäisches Patentamt
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(11) EP 3 241 928 A3

(12) EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
10.01.2018 Bulletin 2018/02

(43) Date of publication A2:
08.11.2017 Bulletin 2017/45

(21) Application number: **17168294.1**

(22) Date of filing: **26.04.2017**

(51) Int Cl.:
C25D 3/06 *(2006.01)* ***C25D 3/10*** *(2006.01)*
C25D 5/18 *(2006.01)* ***C25D 17/10*** *(2006.01)*

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(30) Priority: **02.05.2016 US 201615144688**

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(54) TRIVALENT CHROMIUM PLATING FORMULATIONS AND PROCESSES

(57) An electrolyte solution for chrome plating from trivalent chromium is prepared by dissolving in an aqueous medium a trivalent chromium salt (e.g., chromium (III) chloride or chromium (III) sulfate), dissolving an oxalate compound (e.g., sodium oxalate, potassium oxalate, or oxalic acid), dissolving a metal salt (e.g., aluminum sulfate or aluminum chloride), dissolving an alkali metal sulfate (e.g., sodium sulfate or potassium sulfate), and dissolving an alkali metal halide (e.g., sodium fluoride or potassium fluoride). A substrate is chrome plated from trivalent chromium using the electrolyte solution by passing a current between a cathode and an anode through the electrolyte solution to deposit chromium on the substrate.

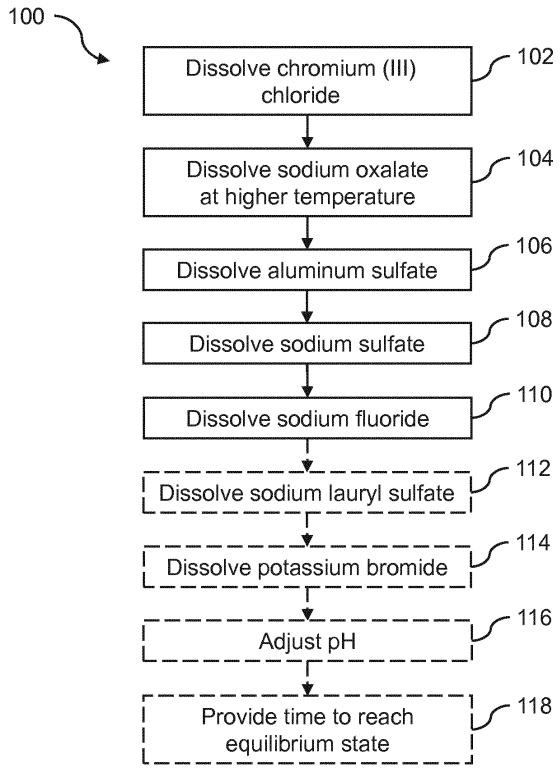

FIG. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 17 16 8294

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	EDIGARYAN A A ET AL: "EFFECT OF FLUORIDE IONS ON CHROMIUM DEPOSITION FROM SULFURIC ACID SOLUTIONS OF CR(III)", PROTECTION OF METALS, PLENUM PUBLISHING CO, NEW YORK, US, vol. 35, no. 1, 1 January 1999 (1999-01-01), pages 1-03, XP000803559, ISSN: 0033-1732 * abstract * * figure 1 * * paragraph "Experimental" * * paragraph "Results and Discussion" *	1-4,15	INV. C25D3/06 C25D3/10 C25D5/18 C25D17/10
X	US 2006/118427 A1 (EDIGARYAN ARAMAYIS [US]) 8 June 2006 (2006-06-08) * abstract * * examples 1, 2 *	1-4,15	
X	EDIGARYAN A A ET AL: "On the Possibility of Replacing Standard Chromium - Plating Electrolytes with Sulfate- Oxalate Solutions of Cr (III)", RUSSIAN JOURNAL OF APPLIED CHEMIS, PLEIADES PUBLISHING / SPRINGER, NEW YORK, NY, US, vol. 76, no. 2, 1 January 2003 (2003-01-01), pages 323-324, XP008082017, ISSN: 1070-4272, DOI: 10.1023/A:1024635603656 * abstract * * paragraph "Experimental" *	15	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	22 August 2017	Lange, Ronny

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

2-4, 15(completely); 1(partially)

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 17 16 8294

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 2-4, 15(completely); 1(partially)

Inventive concept I regards a method for chrome plating a substrate using an electrolyte solution, the method comprising: dissolving in an aqueous medium a trivalent chromium salt in an amount ranging from 0.1 mol to 0.9 mol per liter of the electrolyte solution; dissolving an oxalate compound in an amount ranging from 0.1 mol to 3.0 mol per liter of the electrolyte solution; dissolving a metal salt in an amount ranging from 0.1 mol to 4.0 mol per liter of the electrolyte solution, an alkali metal sulfate in an amount ranging from 0.1 mol to 2.0 mol per liter of the electrolyte solution, and an alkali metal halide in an amount ranging from 0.1 mol to 0.5 mol per liter of the electrolyte solution; and passing a current between a cathode and an anode through the electrolyte solution to deposit chromium on the substrate, wherein the step of dissolving the trivalent chromium salt comprises dissolving chromium (III) chloride and/or chromium (III) sulfate or wherein the step of dissolving the oxalate compound comprises dissolving sodium oxalate in an amount ranging from 0.1 mol to 1.0 mol per liter of the electrolyte solution, potassium oxalate in an amount ranging from 0.1 mol to 1.0 mol per liter of the electrolyte solution, and/or oxalic acid in an amount ranging from 0.1 mol to 3.0 mol per liter of the electrolyte solution and/or wherein dissolving the metal salt comprises dissolving aluminum sulfate in an amount ranging from 0.1 mol to 0.4 mol per liter of the electrolyte solution and/or aluminum chloride in an amount ranging from 0.1 mol to 4.0 mol per liter of the electrolyte solution; dissolving the alkali metal sulfate comprises dissolving sodium sulfate and/or potassium sulfate; and dissolving the alkali metal halide comprises dissolving sodium fluoride and/or potassium fluoride.
1.1.2 Inventive concept I also concerns an electrolyte solution prepared in this way.

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2. claims: 5, 6(completely); 1(partially)

Inventive concept II regards a method for chrome plating a substrate using an electrolyte solution, the method comprising: dissolving in an aqueous medium a trivalent chromium salt in an amount ranging from 0.1 mol to 0.9 mol per liter of the electrolyte solution; dissolving an oxalate compound in an amount ranging from 0.1 mol to 3.0 mol per liter of the electrolyte solution; dissolving a metal salt in an amount ranging from 0.1 mol to 4.0 mol per liter of the electrolyte solution, an alkali metal sulfate in an amount ranging from 0.1 mol to 2.0 mol per liter of the electrolyte solution, and an alkali metal halide in an

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LACK OF UNITY OF INVENTION
SHEET B

Application Number
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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

amount ranging from 0.1 mol to 0.5 mol per liter of the electrolyte solution; and passing a current between a cathode and an anode through the electrolyte solution to deposit chromium on the substrate and wherein the dissolving the trivalent chromium salt, the oxalate compound, the metal salt, the alkali metal sulfate, and the alkali metal halide is performed in the following order: (1) dissolving the trivalent chromium salt and the oxalate compound; (2) dissolving the metal salt; (3) dissolving the alkali metal sulfate; and (4) dissolving the alkali metal halide and/or wherein the step of dissolving the oxalate compound comprises stirring the oxalate compound at a temperature ranging from 70 °C to 80 °C for a time ranging from 1 hour to 3 hours.

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3. claims: 7, 10, 11(completely); 1, 13(partially)

Inventive concept III regards a method for chrome plating a substrate using an electrolyte solution, the method comprising: dissolving in an aqueous medium a trivalent chromium salt in an amount ranging from 0.1 mol to 0.9 mol per liter of the electrolyte solution; dissolving an oxalate compound in an amount ranging from 0.1 mol to 3.0 mol per liter of the electrolyte solution; dissolving a metal salt in an amount ranging from 0.1 mol to 4.0 mol per liter of the electrolyte solution, an alkali metal sulfate in an amount ranging from 0.1 mol to 2.0 mol per liter of the electrolyte solution, and an alkali metal halide in an amount ranging from 0.1 mol to 0.5 mol per liter of the electrolyte solution; and passing a current between a cathode and an anode through the electrolyte solution to deposit chromium on the substrate, wherein the method further comprises adjusting the pH of the electrolyte solution to a pH ranging from 2 to 4 and/or maintaining the electrolyte solution at a pH ranging from 2 to 4 and/or maintaining the electrolyte solution at a temperature ranging from 30 °C to 40 °C during the step of passing the current, wherein the step of passing the current comprises applying a pulsed current or a direct current having a current density ranging from about 5 A/dm 2 to about 50 A/dm 2; and/orthe step of the passing the current comprises applying a pulsed current having a duty cycle ranging from about 20% to about 80%; and/or the step of passing the current is performed until a chromium layer having a thickness greater than 5 microns and hardness greater than 800 HV is formed on the substrate; and/orthe step of passing the current to deposit chromium on the substrate comprises passing the current to deposit chromium on a steel substrate, a copper substrate, a nickel substrate, a copper-coated substrate, or a nickel-coated substrate.

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LACK OF UNITY OF INVENTION
SHEET B

Application Number
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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

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4. claims: 8, 9, 12, 14(completely); 1, 13(partially)

Inventive concept IV regards a method for chrome plating a substrate using an electrolyte solution, the method comprising: dissolving in an aqueous medium a trivalent chromium salt in an amount ranging from 0.1 mol to 0.9 mol per liter of the electrolyte solution; dissolving an oxalate compound in an amount ranging from 0.1 mol to 3.0 mol per liter of the electrolyte solution; dissolving a metal salt in an amount ranging from 0.1 mol to 4.0 mol per liter of the electrolyte solution, an alkali metal sulfate in an amount ranging from 0.1 mol to 2.0 mol per liter of the electrolyte solution, and an alkali metal halide in an amount ranging from 0.1 mol to 0.5 mol per liter of the electrolyte solution; and passing a current between a cathode and an anode through the electrolyte solution to deposit chromium on the substrate, the method further comprising adding sodium lauryl sulfate and/or potassium lauryl sulfate in an amount ranging from 0.1 g to 1 g per liter of the electrolyte solution and/or adding sodium bromide and/or potassium bromide in an amount ranging from 0.1 g to 1 g per liter of the electrolyte solution and/or wherein the step of passing the current is performed using a carbonaceous anode, a platinum anode, or a platinized titanium anode, and wherein the trivalent chromium salt comprises chromium (III) sulfate and/or wherein: the step of passing the current is performed using a carbonaceous anode, and wherein the trivalent chromium salt comprises chromium (III) chloride.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 17 16 8294

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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22-08-2017

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		US 2006118427 A1	08-06-2006
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