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(54) Functional chromium layer with improved corrosion resistance

Funktionelle Chromschicht mit verbesserter Korrosionsbeständigkeit

Couche de chrome fonctionnel présentant une résistance améliorée à la corrosion

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Description

Field of the Invention

5 [0001] The present invention relates to plating bath compositions and a process for depositing functional chromium layers by electroplating.

Background of the Invention

10 [0002] Functional chromium layers deposited by electroplating are used to improve wear and corrosion resistance of products such as shock absorbers, hydraulic pistons and the like.

[0003] The plating bath compositions used comprise chromic acid, sulfate ions, water and an alkyl-sulfonic acid or salt thereof.

15 [0004] Alkyl-sulfonic acid catalysts having a molar ratio $S : C \geq 1 : 3$ are disclosed in EP 0 196 053 B1. Examples of suitable alkyl-sulfonic acids are methyl-sulfonic acid, ethyl-sulfonic acid, propyl-sulfonic acid, methane-disulfonic acid and 1,2-ethane-disulfonic acid. Said alkyl-sulfonic acids improve the cathodic current efficiency during plating.

[0005] The use of alkyl-polysulfonic acids, halogenated alkyl-polysulfonic acids and corresponding salts such as methane-disulfonic acid for reducing the corrosion of lead anodes during plating is disclosed in EP 0 452 471 B1.

20 [0006] Aromatic-trisulfonic acids as an additive in plating bath compositions for depositing functional chromium layers are disclosed in US 2,195,409. The chromium layers obtained from such plating bath compositions are bright and uniform.

[0007] A plating bath composition for depositing a functional chromium layer with an improved cathodic current efficiency comprising propane-1,2,3-trisulfonic acid is disclosed in DE 43 05 732 A1.

Objective of the present Invention

25 [0008] The objective of the present invention is to provide a plating bath composition and a process utilizing said plating bath composition for depositing functional chromium layers having an improved corrosion resistance.

Summary of the Invention

30 [0009] This objective is solved with an aqueous electroplating bath for depositing a functional chromium layer, comprising

(i) a source for chromium(VI) ions,

35 (ii) a source for sulfate ions and

(iii) methane-trisulfonic acid or a salt thereof.

40 [0010] This objective is further solved with a process for depositing a functional chromium layer onto a metallic substrate, comprising, in this order, the steps of

(i) providing a metallic substrate,

45 (ii) contacting said substrate with an aqueous electroplating bath comprising a source for chromium(VI) ions, a source for sulfate ions and methane-trisulfonic acid or a salt thereof and

(iii) applying an external current to said substrate as the cathode and thereby depositing a functional chromium layer onto said substrate.

50 [0011] The functional chromium layers deposited from the aqueous plating bath and by the process according to the present invention have an increased corrosion resistance compared to functional chromium layers deposited from conventional electroplating bath compositions comprising known alkyl-sulfonic acid.

Detailed Description of the Invention

55 [0012] The aqueous electroplating bath according to the present invention comprises a source for chromium(VI) ions, sulfate ions, methane-trisulfonic acid, or a salt thereof, and optionally a surface active agent.

[0013] The source for chromium(VI) ions is preferably a chromium(VI) compound soluble in the plating bath such as CrO_3 , $\text{Na}_2\text{Cr}_2\text{O}_7$ and $\text{K}_2\text{Cr}_2\text{O}_7$, most preferably CrO_3 . The concentration of chromium(VI) ions in the electroplating bath according to the present invention preferably ranges from 80 to 600 g/l, more preferably from 100 to 200 g/l.

[0014] Sulfate ions present in the electroplating bath are preferably added in form of sulfuric acid or a plating bath soluble sulfate salt such as Na_2SO_4 . The concentration of sulfate ions in the electroplating bath preferably ranges from 1 to 15 g/l, more preferably from 2 to 6 g/l.

[0015] The ratio of the concentration in wt.-% of chromic acid to sulfate preferably ranges from 25 to 200, more preferably from 60 to 150.

[0016] The alkyl-sulfonic acid in the electroplating bath is either methane-trisulfonic acid ($\text{HC}(\text{SO}_2\text{OH})_3$) or a mixture of methane-trisulfonic acid and other alkyl-sulfonic acids. Corresponding salts such as sodium, potassium and ammonium salts of the aforementioned sulfonic acids can also be employed instead of or as a mixture with the free alkyl-sulfonic acids.

[0017] A precursor of methane-trisulfonic acid or a salt thereof which is oxidized in the electroplating bath according to the present invention to methane-trisulfonic acid or a salt thereof may be used as part or sole source of methane-trisulfonic acid or a salt thereof.

[0018] The concentration of methane-trisulfonic acid or a salt thereof in the plating bath according to the present invention preferably ranges from 6 to 80 mmol/l, more preferably from 12 to 60 mmol/l.

[0019] The overall concentration of methane-trisulfonic acid and other alkyl-sulfonic acids or salts of the aforementioned in case a mixture of alkyl-sulfonic acids is employed preferably ranges from 12 to 160 mmol/l, more preferably from 24 to 120 mmol/l.

[0020] A high number of micro-cracks inside the functional chromium layer deposited is desired because thereby a high corrosion resistance and desirable mechanical properties such as a reduced internal stress are achieved. Micro-cracks in contrast to macro-cracks within a functional chromium layer do not extend to the surface of the underlying substrate and thus do not result in corrosion of the underlying substrate material, which usually is steel.

[0021] Methane-trisulfonic acid or a salt thereof or constituent of a mixture with other alkyl-sulfonic acid(s) enables a high number of desired micro-cracks in the range of 200 to 1000, more preferably 450 to 750 micro-cracks per cm of the functional chromium layer surface as determined after etching in an aqueous solution containing sodium hydroxide and $\text{K}_3[\text{Fe}(\text{CN})_6]$ with an optical microscope. The number of micro-cracks along lines is counted and the number of micro-cracks per cm is then calculated with the formula

$$\text{Micro-cracks per cm} = (\text{average number of cracks per line}) : (\text{length of line in cm})$$

[0022] The number of micro-cracks and the corrosion resistance is increased with methane-trisulfonic acid or a salt thereof as the catalyst compared with methane-disulfonic acid sodium salt or propane-1,2,3-trisulfonic acid sodium salt as the sole alkyl-sulfonic acid. This is shown in Examples 1 to 3.

[0023] Furthermore, an increased number of desired micro-cracks is also obtained at higher current densities (Example 3) whereas the number of micro-cracks is decreasing at higher current densities in case of known alkyl-sulfonic acids such as methane-disulfonic acid (Example 1). Higher current density values during plating are desired because the plating speed is increased thereby.

[0024] The electroplating bath according to the present invention optionally further comprises a surface active agent which reduces formation of undesired foam on top of the plating liquid. The surface active additive is selected from the group comprising perfluorinated sulfonate tenisdes, perfluorinated phosphate ten-sides, perfluorinated phosphonate tensides, partially fluorinated sulfonate ten-sides, partially fluorinated phosphate tensides, partially fluorinated phosphonate tensides and mixtures thereof.

[0025] The concentration of the optional surface active agent preferably ranges from 0.05 to 4 g/l, more preferably from 0.1 to 2.5 g/l.

[0026] The current density applied during plating preferably ranges from 10 to 250 A/dm², more preferably from 40 to 200 A/dm². The substrate to be plated with a functional chromium layer serves as the cathode during electroplating.

[0027] Cathodic current efficiency is the percentage of current, which is actually used for the deposition of the metal (chromium) at the cathode during electroplating of the functional chromium layer.

[0028] The preferred current efficiency of the process according to the present invention is $\geq 22\%$ at a current density of 50 A/dm².

[0029] The temperature of the electroplating bath according to the present invention is held during plating preferably in a range of 10 to 80 °C, more preferably in a range of 45 to 70 °C and most preferably from 50 to 60 °C.

[0030] Inert anodes are preferably applied in the process according to the present invention.

[0031] Suitable inert anodes are for example made of titanium or a titanium alloy coated with one or more platinum group metal, alloys thereof and/or oxides thereof. The coating preferably consists of platinum metal, iridium oxide or a

mixture thereof. Such inert anodes enable higher current densities during electroplating and thereby a higher plating rate compared to lead anodes.

[0032] The plating bath according to the present invention can also be operated with conventional lead anodes.

[0033] Chromium(III) ions are formed when using such inert anodes. Methane-trisulfonic acid and/or a salt thereof as the alkyl-sulfonic acid in a chromium(VI) ion based functional chromium electroplating bath is very sensitive to chromium(III) ions.

[0034] In a preferred embodiment of the present invention, cations of a further metal such as silver ions, lead ions and mixtures thereof are added to the electroplating bath. Thereby, the negative impact of chromium(III) ions can be minimized. The concentration of ions of a further metal preferably ranges from 0.005 to 5 g/l, more preferably from 0.01 to 3 g/l.

[0035] The present invention provides a functional chromium electroplating bath and a process for depositing a functional chromium layer onto a substrate having an increased corrosion resistance which is also obtained at high current densities.

Examples

[0036] The invention will now be illustrated by reference to the following non-limiting examples.

[0037] The number of micro-cracks was determined with an optical microscope after etching the surface of the chromium layer in an aqueous solution containing sodium hydroxide and $K_3[Fe(CN)_6]$. The number of micro-cracks along several lines having the same length is determined from which the average number of micro-cracks is calculated and then divided by the line length given in cm to provide the "average number of micro-cracks" in cracks/cm.

[0038] The corrosion resistance of the functional chromium layers was determined according to ISO 9227 NSS (neutral salt spray test).

[0039] An aqueous electroplating bath stock solution containing 250 g/l CrO_3 , 3.2 g/l sulfate ions and 2 ml/l of a surface active agent was used throughout examples 1 to 3. Different amounts of alkyl-sulfonic acids were added to this stock solution prior to depositing the functional chromium layers.

Example 1 (comparative)

[0040] The alkyl-sulfonic acid was methane-disulfonic acid disodium salt added to the stock solution in a concentration of 2 to 12 g/l (7.6 to 45.4 mmol/l). This alkyl-sulfonic acid is disclosed in EP 0 452 471 B1.

Table 1 summarizes the average number of micro-cracks determined at different concentrations of methane-disulfonic acid disodium salt as the sole alkyl-sulfonic acid (plating bath temperature: 58 °C, current density: 50 A/dm²).

Catalyst (mmol/l)	concentration	Current efficiency (%)	Average number of micro-cracks (crack/cm)
7.6		24.6	600
15.2		24.3	820
22.7		22.2	820
30.3		19.7	660
37.9		20.3	530
45.4		18.9	440

[0041] A high number of desired micro-cracks is only obtained when a narrow concentration range of the catalyst methane-disulfonic acid disodium salt is used in the stock solution.

Table 2 summarizes the average number of micro-cracks determined at different current densities for an electroplating bath composition with 18.9 mmol/l (5 g/l) methane-disulfonic acid disodium salt as the sole alkyl-sulfonic acid.

Current density (A/dm ²)	Current efficiency (%)	Average number of micro-cracks (crack/cm)
30	21.7	730
40	23.7	660
50	24.4	630
60	25.3	620
70	25.9	580

[0042] The number of desired micro-cracks is declining with increased current density.

[0043] Formation of undesired red rust was determined after 192 h of neutral salt spray test according to ISO 9227 NSS (> 0.1 % of the surface area covered with red rust after 192 h).

Example 2 (comparative)

[0044] The alkyl-sulfonic acid was propane-1,2,3-trisulfonic acid trisodium salt added to the stock solution in a concentration of 14.3 mmol/l (5 g/l). This alkyl-disulfonic acid is disclosed in DE 43 05 732 A1.

[0045] The current efficiency at 50 A/dm² and a plating bath temperature of 55 °C is 17.4 % and the number of micro-cracks in the chromium layer deposited under these conditions is 160 cracks/cm.

[0046] Formation of undesired red rust was already determined after 24 h of neutral salt spray test according to ISO 9227 NSS (> 0.1 % of the surface area covered with red rust after 24 h).

Example 3 (invention)

[0047] The alkyl-sulfonic acid was methane-trisulfonic acid trisodium salt added to the stock solution in concentrations of 6.2 to 37.2 mmol/l (2 to 12 g/l).

Table 3 summarizes the average number of micro-cracks determined at different concentrations of methane-trisulfonic acid trisodium salt as the sole alkyl-sulfonic acid (plating bath temperature: 58 °C, current density: 50 A/dm²).

Catalyst concentration (mmol/l)	Current efficiency (%)	Average number of micro-cracks (crack/cm)
6.2	23.6	270
12.4	24.5	670
18.6	24.3	950
24.8	23.7	1020
31.0	23.8	920
37.2	22.9	1020

Table 4 summarizes the average number of micro-cracks determined at different current densities for an electroplating bath composition with 24.8 mmol/l (8 g/l) methane-trisulfonic acid trisodium salt as the sole alkyl-sulfonic acid.

Current density (A/dm ²)	Current efficiency (%)	Average number of micro-cracks (crack/cm)
30	19.4	810
40	23.2	780
50	24.8	860
60	26.0	850
70	27.2	840

[0048] A high number of desired micro-cracks was obtained in the whole current density range applied.

[0049] Formation of undesired red rust was not determined until 552 h of neutral salt spray test according to ISO 9227 NSS.

Claims

1. An aqueous electroplating bath for depositing a functional chromium layer, comprising

- (i) a source for chromium(VI) ions,
- (ii) a source for sulfate ions and
- (iii) methane-trisulfonic acid or a salt thereof.

2. The aqueous electroplating bath for depositing a functional chromium layer according to claim 1 wherein the con-

centration of chromium(VI) ions ranges from 80 to 600 g/l.

3. The aqueous electroplating bath for depositing a functional chromium layer according to any of the foregoing claims wherein the concentration of sulfate ions ranges from 1 to 15 g/l.
4. The aqueous electroplating bath for depositing a functional chromium layer according to any of the foregoing claims wherein the salt of methane-trisulfonic acid is selected from sodium, potassium and ammonium salts.
5. The aqueous electroplating bath for depositing a functional chromium layer according to any of the foregoing claims wherein the concentration of methane-trisulfonic acid or a salt thereof ranges from 6 to 80 mmol/l.
6. The aqueous electroplating bath for depositing a functional chromium layer according to any of the foregoing claims wherein the plating bath further comprises a surface active agent which is selected from the group consisting of perfluorinated sulfonate tensides, perfluorinated phosphate tensides, perfluorinated phosphonate tensides, partially fluorinated sulfonate tensides, partially fluorinated phosphate tensides, partially fluorinated phosphonate tensides and mixtures thereof.
7. The aqueous electroplating bath for depositing a functional chromium layer according to claim 6 wherein the concentration of the surface active agent ranges from 0.05 to 4 g/l.
8. A process for depositing a functional chromium layer onto a metallic substrate comprising, in this order, the steps of
 - (i) providing a metallic substrate,
 - (ii) contacting said substrate with the aqueous electroplating bath according to any of claims 1 to 7 and
 - (iii) applying an external current to said substrate as the cathode and thereby depositing a functional chromium layer onto said substrate.
9. The process for depositing a functional chromium layer onto a metallic substrate according to claim 8 wherein the aqueous electroplating bath is held at a temperature in the range of 10 to 80 °C during use.
10. The process for depositing a functional chromium layer onto a metallic substrate according to claims 8 and 9 wherein a current density in the range of 10 to 250 A/dm² is applied to the metallic substrate during use.
11. The process for depositing a functional chromium layer onto a metallic substrate according to any of claims 8 to 10 wherein an inert anode is used in step (iii).
12. The process for depositing a functional chromium layer onto a metallic substrate according to claim 11 wherein the inert anode has a surface selected from the group consisting of platinum metal, iridium oxide and mixtures thereof.
13. The process for depositing a functional chromium layer onto a metallic substrate according to any of claims 11 and 12 wherein the aqueous electroplating bath further comprises cations of an additional metal selected from the group consisting of silver, lead and mixtures thereof.
14. The process for depositing a functional chromium layer onto a metallic substrate according to claim 13 wherein the concentration of the cations of an additional metal ranges from 0.005 to 5 g/l.
15. Use of methane-trisulfonic acid or a salt thereof as the catalyst in an aqueous electroplating bath comprising a source for chromium(VI) ions and sulfate ions for depositing functional chromium layers with an increased corrosion resistance.

Patentansprüche

1. Wässriges galvanisches Bad zur Abscheidung einer funktionalen Chromschicht, umfassend
 - (i) eine Quelle für Chrom(VI)-Ionen,
 - (ii) eine Quelle für Sulfationen und
 - (iii) Methantrisulfonsäure oder ein Salz davon.

2. Wässriges galvanisches Bad zur Abscheidung einer funktionalen Chromschicht nach Anspruch 1, wobei die Konzentration von Chrom(VI)-Ionen im Bereich von 80 bis 600 g/l liegt.
3. Wässriges galvanisches Bad zur Abscheidung einer funktionalen Chromschicht nach einem der vorhergehenden Ansprüche, wobei die Konzentration von Sulfationen im Bereich von 1 bis 15 g/l liegt.
4. Wässriges galvanisches Bad zur Abscheidung einer funktionalen Chromschicht nach einem der vorhergehenden Ansprüche, wobei das Salz von Methantrisulfonsäure aus Natrium-, Kalium- und Ammoniumsalzen ausgewählt ist.
5. Wässriges galvanisches Bad zur Abscheidung einer funktionalen Chromschicht nach einem der vorhergehenden Ansprüche, wobei die Konzentration von Methantrisulfonsäure oder einem Salz davon im Bereich von 6 bis 80 mmol/l liegt.
6. Wässriges galvanisches Bad zur Abscheidung einer funktionalen Chromschicht nach einem der vorhergehenden Ansprüche, wobei das galvanische Bad ferner eine oberflächenaktive Verbindung umfasst, das aus der Gruppe bestehend aus perfluorierten Sulfonat-Tensiden, perfluorierten Phosphat-Tensiden, perfluorierten Phosphonat-Tensiden, teilfluorierten Sulfonat-Tensiden, teilfluorierten Phosphat-Tensiden, teilfluorierten Phosphonat-Tensiden und Mischungen davon ausgewählt ist.
7. Wässriges galvanisches Bad zur Abscheidung einer funktionalen Chromschicht nach Anspruch 6, wobei die Konzentration der oberflächenaktiven Verbindung im Bereich von 0,05 bis 4 g/l liegt.
8. Verfahren zur Abscheidung einer funktionalen Chromschicht auf einem Metallsubstrat, umfassend folgende Schritte in der angegebenen Reihenfolge:
 - (i) Bereitstellen eines Metallsubstrats,
 - (ii) Inberührungbringen des Substrats mit dem wässrigen galvanischen Bad nach einem der Ansprüche 1 bis 7 und
 - (iii) Anlegen eines externen Stroms an das Substrat als Kathode und dadurch Abscheiden einer funktionalen Chromschicht auf dem Substrat.
9. Verfahren zur Abscheidung einer funktionalen Chromschicht auf einem Metallsubstrat nach Anspruch 8, wobei das wässrige galvanische Bad bei der Verwendung bei einer Temperatur im Bereich von 10 bis 80°C gehalten wird.
10. Verfahren zur Abscheidung einer funktionalen Chromschicht auf einem Metallsubstrat nach den Ansprüchen 8 und 9, wobei bei der Verwendung eine Stromdichte von 10 bis 250 A/dm² an das Metallsubstrat angelegt wird.
11. Verfahren zur Abscheidung einer funktionalen Chromschicht auf einem Metallsubstrat nach einem der Ansprüche 8 bis 10, wobei in Schritt (iii) eine inerte Anode verwendet wird.
12. Verfahren zur Abscheidung einer funktionalen Chromschicht auf einem Metallsubstrat nach Anspruch 11, wobei die inerte Anode eine Oberfläche aus der Gruppe bestehend aus Platinmetall, Iridiumoxid und Mischungen davon aufweist.
13. Verfahren zur Abscheidung einer funktionalen Chromschicht auf einem Metallsubstrat nach einem der Ansprüche 11 und 12, wobei das wässrige galvanische Bad ferner Kationen eines zusätzlichen Metalls aus der Gruppe bestehend aus Silber, Blei und Mischungen davon umfasst.
14. Verfahren zur Abscheidung einer funktionalen Chromschicht auf einem Metallsubstrat nach Anspruch 13, wobei die Konzentration der Kationen eines zusätzlichen Metalls im Bereich von 0,005 bis 5 g/l liegt.
15. Verwendung von Methantrisulfonsäure oder einem Salz davon als Katalysator in einem wässrigen galvanischen Bad, das eine Quelle für Chrom(VI)-Ionen und Sulfationen umfasst, zum Abscheiden von funktionalen Chromschichten mit erhöhter Korrosionsbeständigkeit.

Revendications

1. Bain aqueux de dépôt électrolytique pour le dépôt d'une couche de chrome fonctionnelle, comprenant
 - (i) une source d'ions chrome (VI),
 - (ii) une source d'ions sulfate, et
 - (iii) de l'acide méthane-trisulfonique ou un sel de celui-ci.
2. Bain aqueux de dépôt électrolytique pour le dépôt d'une couche de chrome fonctionnelle selon la revendication 1 dans lequel la concentration en ions chrome (VI) va de 80 à 600 g/l.
3. Bain aqueux de dépôt électrolytique pour le dépôt d'une couche de chrome fonctionnelle selon l'une quelconque des revendications précédentes dans lequel la concentration en ions sulfate va de 1 à 15 g/l.
4. Bain aqueux de dépôt électrolytique pour le dépôt d'une couche de chrome fonctionnelle selon l'une quelconque des revendications précédentes dans lequel le sel d'acide méthane-trisulfonique est choisi parmi les sels de sodium, potassium et ammonium.
5. Bain aqueux de dépôt électrolytique pour le dépôt d'une couche de chrome fonctionnelle selon l'une quelconque des revendications précédentes dans lequel la concentration d'acide méthane-trisulfonique ou d'un sel de celui-ci va de 6 à 80 mmol/l.
6. Bain aqueux de dépôt électrolytique pour le dépôt d'une couche de chrome fonctionnelle selon l'une quelconque des revendications précédentes, le bain de dépôt comprenant en outre un agent de surface qui est choisi dans le groupe constitué par les tensioactifs au sulfonate perfluoré, les tensioactifs au phosphate perfluoré, les tensioactifs au phosphonate perfluoré, les tensioactifs au sulfonate partiellement fluoré, les tensioactifs au phosphate partiellement fluoré, les tensioactifs au phosphonate partiellement fluoré et les mélanges de ceux-ci.
7. Bain aqueux de dépôt électrolytique pour le dépôt d'une couche de chrome fonctionnelle selon la revendication 6 dans lequel la concentration de l'agent de surface va de 0,05 à 4 g/l.
8. Procédé de dépôt d'une couche de chrome fonctionnelle sur un substrat métallique comprenant, dans cet ordre, les étapes consistant à
 - (i) se procurer un substrat métallique,
 - (ii) mettre ledit substrat en contact avec le bain aqueux de dépôt électrolytique selon l'une quelconque des revendications 1 à 7, et
 - (iii) appliquer un courant externe audit substrat en tant que cathode et déposer ainsi une couche de chrome fonctionnelle sur ledit substrat.
9. Procédé de dépôt d'une couche de chrome fonctionnelle sur un substrat métallique selon la revendication 8 dans lequel le bain aqueux de dépôt électrolytique est maintenu à une température dans la gamme de 10 à 80 °C pendant l'utilisation.
10. Procédé de dépôt d'une couche de chrome fonctionnelle sur un substrat métallique selon les revendications 8 et 9 dans lequel une densité de courant dans la gamme de 10 à 250 A/dm² est appliquée au substrat métallique pendant l'utilisation.
11. Procédé de dépôt d'une couche de chrome fonctionnelle sur un substrat métallique selon l'une quelconque des revendications 8 à 10 dans lequel une anode inerte est utilisée à l'étape (iii).
12. Procédé de dépôt d'une couche de chrome fonctionnelle sur un substrat métallique selon la revendication 11 dans lequel l'anode inerte a une surface choisie dans le groupe constitué par le platine métallique, l'oxyde d'iridium et les mélanges de ceux-ci.
13. Procédé de dépôt d'une couche de chrome fonctionnelle sur un substrat métallique selon l'une quelconque des revendications 11 et 12 dans lequel le bain aqueux de dépôt électrolytique comprend en outre des cations d'un métal supplémentaire choisi dans le groupe constitué par l'argent, le plomb et les mélanges de ceux-ci.

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14. Procédé de dépôt d'une couche de chrome fonctionnelle sur un substrat métallique selon la revendication 13 dans lequel la concentration des cations d'un métal supplémentaire va de 0,005 à 5 g/l.
- 5 15. Utilisation d'acide méthane-trisulfonique ou d'un sel de celui-ci comme catalyseur dans un bain aqueux de dépôt électrolytique comprenant une source d'ions chrome (VI) et d'ions sulfate pour le dépôt de couches de chrome fonctionnelles avec une résistance accrue à la corrosion.

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REFERENCES CITED IN THE DESCRIPTION

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