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(54) **Title:** FUNCTIONAL CHROMIUM LAYER WITH IMPROVED CORROSION RESISTANCE

(57) **Abstract:** The aqueous electroplating bath according to the present invention comprises chromium(VI) ions, sulfate ions and methane-trisulfonic acid or a salt thereof as the catalyst. The functional chromium layer deposited from the aqueous electroplating bath according to the present invention has an increased corrosion resistance.



WO 2014/170037 A1

Functional chromium layer with improved corrosion resistance

5 **Field of the Invention**

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

Background of the Invention

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

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

Alkyl-sulfonic acid catalysts having a molar ratio $S : C \geq 1 : 3$ are disclosed in
15 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.

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

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.

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

- 5 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

This objective is solved with an aqueous electroplating bath for depositing a
10 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.

This objective is further solved with a process for depositing a functional chro-
15 mium layer onto a metallic substrate, comprising, in this order, the steps of

- (i) providing a metallic substrate,
- (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
- 20 (iii) applying an external current to said substrate as the cathode and thereby depositing a functional chromium layer onto said substrate.

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.

5 **Detailed Description of the Invention**

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.

10 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.

15 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.

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

20 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 one or more other alkyl-sulfonic acids. Suitable other alkyl-sulfonic acids in mixtures with methane-trisulfonic acid comprise methane-sulfonic acid, methane-disulfonic acid, ethane-sulfonic acid, 1,2-ethane-disulfonic acid, propyl sulfonic acid, 1,2-
25 propane-disulfonic acid, 1,3-propane-disulfonic acid and 1,2,3-propane-trisulfonic acid. 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.

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
5 or a salt thereof may be used as part or sole source of methane-trisulfonic acid or a salt thereof.

The concentration of methane-trisulfonic acid or a salt thereof in the plating bath according to the present invention preferably ranges from 2 to 80 mmol/l, more preferably from 4 to 60 mmol/l.

10 The overall concentration of methane-trisulfonic acid and other alkyl-sulfonic acids or salts of the aforementioned in case a mixture of methane-trisulfonic acid with other alkyl-sulfonic acids is employed preferably ranges from 4 to 160 mmol/l, more preferably from 12 to 120 mmol/l.

A high number of micro-cracks inside the functional chromium layer deposited is
15 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.

20 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 $K_3[Fe(CN)_6]$ with an optical micro-
25 scope. The number of micro-cracks along lines is counted and the number of micro-cracks per cm is then calculated with the formula

Micro-cracks per cm = (average number of cracks per line) : (length of line in cm)

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.

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.

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 tensides, perfluorinated phosphate tensides, perfluorinated phosphonate tensides, partially fluorinated sulfonate tensides, partially fluorinated phosphate tensides, partially fluorinated phosphonate tensides and mixtures thereof.

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.

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.

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.

The preferred current efficiency of the process according to the present invention is $\geq 22\%$ at a current density of 50 A/dm^2 .

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 .

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

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.

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

Chromium(III) ions are formed when using such inert anodes. Methanesulfonic 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.

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 .

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

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

5 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.

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

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)

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.

20 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 concentration (mmol/l)	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

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

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

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)

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.

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.

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)

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

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

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,
 - 5 (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 concentration of chromium(VI) ions ranges from 80 to 600 g/l.
- 10 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.
15
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 2 to 80 mmol/l.
- 20 6. The aqueous electroplating bath for depositing a functional chromium layer according to any of the foregoing claims comprising methane-trisulfonic acid and one or more other alkyl-sulfonic acids selected from the group comprising methane-sulfonic acid, methane-disulfonic acid, ethane-sulfonic acid, 1,2-ethane-disulfonic acid, propyl sulfonic acid, 1,2-

propane-disulfonic acid, 1,3-propane-disulfonic acid and 1,2,3-propane-trisulfonic acid.

7. 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.

8. The aqueous electroplating bath for depositing a functional chromium layer according to claim 7 wherein the concentration of the surface active agent ranges from 0.05 to 4 g/l.

9. 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 8 and
- (iii) applying an external current to said substrate as the cathode and thereby depositing a functional chromium layer onto said substrate.

10. The process for depositing a functional chromium layer onto a metallic substrate according to claim 9 wherein the aqueous electroplating bath is held at a temperature in the range of 10 to 80 °C during use.

11. The process for depositing a functional chromium layer onto a metallic substrate according to claims 9 and 10 wherein a current density in the range of 10 to 250 A/dm² is applied to the metallic substrate during use.

5 12. The process for depositing a functional chromium layer onto a metallic substrate according to any of claims 9 to 11 wherein an inert anode is used in step (iii).

10 13. The process for depositing a functional chromium layer onto a metallic substrate according to claim 12 wherein the inert anode has a surface selected from the group consisting of platinum metal, iridium oxide and mixtures thereof.

14. The process for depositing a functional chromium layer onto a metallic substrate according to any of claims 12 and 13 wherein the aqueous electroplating bath further comprises cations of an additional metal selected from the group consisting of silver, lead and mixtures thereof.

15 15. The process for depositing a functional chromium layer onto a metallic substrate according to claim 14 wherein the concentration of the cations of an additional metal ranges from 0.005 to 5 g/l.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/051251

A. CLASSIFICATION OF SUBJECT MATTER

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ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25D C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 196 053 A2 (M & T CHEMICALS INC [US]) 1 October 1986 (1986-10-01) cited in the application the whole document -----	1-15
A	DE 43 05 732 A1 (TRINOVA CHEMIE GMBH [DE]) 22 September 1994 (1994-09-22) cited in the application the whole document -----	1-15
A	US 5 453 175 A (NEWBY KENNETH R [US]) 26 September 1995 (1995-09-26) the whole document -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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