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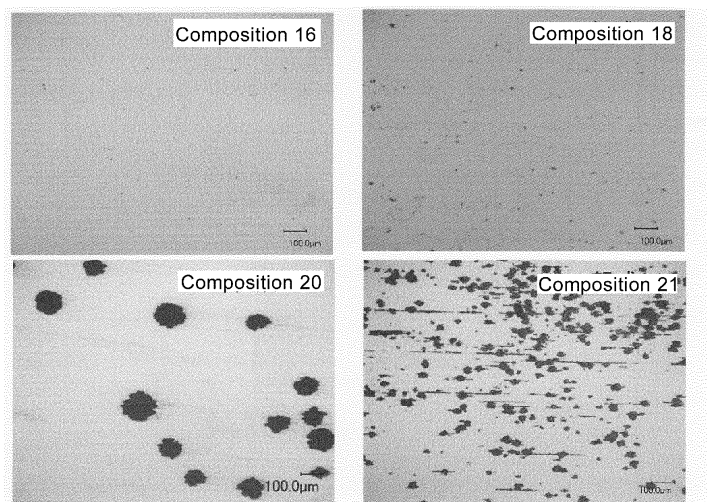
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(54) **TRIVALENT CHROMIUM PLATING SOLUTION AND METHOD FOR CHROMIUM-PLATING USING SAME**

(57) A trivalent chromium plating solution having a high plating deposition rate and being practical is provided with a trivalent chromium plating solution containing a trivalent chromium compound, a complexing agent, potassium sulfate and ammonium sulfate as a conductive salt, a pH buffer, and a sulfur-containing organic com-

pound, containing a carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof as the complexing agent, and containing a combination of saccharin or a salt thereof and a sulfur-containing organic compound having an allyl group as the sulfur-containing organic compound.

[FIG. 3]



Description

Technical Field

5 **[0001]** The present invention relates to a trivalent chromium plating solution and a method for chromium-plating using the same.

Background Art

10 **[0002]** Chromium plating is used as a coating film for decoration owing to the silvery white color thereof. Hexavalent chromium has been used for the chromium plating, but the use of hexavalent chromium is restricted in recent years due to the environmental implications thereof, and the technology is shifted to the use of trivalent chromium.

[0003] Many reports have been made for the technique using trivalent chromium, and for example, a chromium electrolytic plating solution containing a water soluble trivalent chromium salt, a complexing agent for a trivalent chromium ion, such as malic acid, a pH buffering compound, a sulfur-containing organic compound, such as thiourea, and a water soluble compound, such as saccharin, and having pH of from 2.8 to 4.2 has been known (PTL 1).

[0004] However, this trivalent chromium plating solution has a low plating deposition rate and thus is not practical.

Citation List

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Patent Literature

[0005] PTL 1: Japanese Patent No. 5,696,134

25 Summary of Invention

Technical Problem

30 **[0006]** An object of the present invention is to provide a trivalent chromium plating solution that has a high plating deposition rate and is practical.

Solution to Problem

35 **[0007]** As a result of the earnest investigations by the present inventors, it has been found that a trivalent chromium plating solution can have a high plating deposition rate and can be practical by using a carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof as a complexing agent for a trivalent chromium ion, and in addition, using a combination of saccharin or a salt thereof and a compound having an allyl group as a sulfur-containing organic compound, and thus the present invention has been completed.

40 **[0008]** Accordingly, the present invention relates to a trivalent chromium plating solution containing a trivalent chromium compound, a complexing agent, potassium sulfate and ammonium sulfate as a conductive salt, a pH buffer, and a sulfur-containing organic compound, containing a carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof as the complexing agent, and containing a combination of saccharin or a salt thereof and a sulfur-containing organic compound having an allyl group as the sulfur-containing organic compound.

45 **[0009]** The present invention also relates to a method for chromium-plating on an article to be plated, including electroplating an article to be plated with the trivalent chromium plating solution.

[0010] The present invention further relates to a chromium-plated product including an article to be plated, electroplated with the trivalent chromium plating solution.

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Advantageous Effects of Invention

55 **[0011]** The trivalent chromium plating solution of the present invention provides an appearance that is equivalent to plating with hexavalent chromium despite the plating with trivalent chromium, and furthermore has a high plating deposition rate and is practical.

Brief Description of Drawings

[0012]

Fig. 1 is an illustration showing the position where the throwing distance is measured in the Hull cell test of Example 1.
 Fig. 2 is a graph showing the relationship between the ratio of potassium sulfate and ammonium sulfate contained in the trivalent chromium plating solution and the throwing power in the Hull cell test of Example 1.
 Fig. 3 is images showing the results of the corrosion resistance test (CASS test).

Description of Embodiments

[0013] The trivalent chromium plating solution of the present invention (which may be hereinafter referred to as a "plating solution of the present invention") is a trivalent chromium plating solution that contains a trivalent chromium compound, a complexing agent, potassium sulfate and ammonium sulfate as a conductive salt, a pH buffer, and a sulfur-containing organic compound,
 contains a carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof as the complexing agent, and
 contains a combination of saccharin or a salt thereof and a sulfur-containing organic compound having an allyl group as the sulfur-containing organic compound.

[0014] The trivalent chromium compound used in the plating solution of the present invention is not particularly limited, examples of which include basic chromium sulfate, chromium sulfate, chromium chloride, chromium sulfamate, and chromium acetate, and basic chromium sulfate and chromium sulfate are preferred. The trivalent chromium compound may be used alone or as a combination of two or more kinds thereof. The content of the trivalent chromium compound in the plating solution of the present invention is not particularly limited, and for example, is from 1 to 25 g/L, and preferably from 5 to 15 g/L, in terms of metallic chromium.

[0015] The complexing agent used in the plating solution of the present invention is a carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof. Examples of the complexing agent include a carboxylic acid, such as tartaric acid, and a salt of the carboxylic acid, such as diammonium tartrate, Rochelle salt, and sodium tartrate. The complexing agent may be used alone or as a combination of two or more kinds thereof. The content of the carboxylic acid or a salt thereof in the plating solution of the present invention is not particularly limited, and for example, is from 5 to 90 g/L, and preferably from 10 to 60 g/L. In the present invention, the hydroxy group in the carboxy group is not counted as the hydroxy group.

[0016] The conductive salt used in the plating solution of the present invention is potassium sulfate and ammonium sulfate. The content of potassium sulfate and ammonium sulfate in the plating solution of the present invention is not particularly limited, and for example, is from 100 to 300 g/L, and preferably from 120 to 240 g/L, in terms of total amount. The mass ratio of potassium sulfate and ammonium sulfate ((potassium sulfate) / (ammonium sulfate)) may be from 0.5 to 60, and preferably from 1.0 to 30. In the case where the mass ratio (potassium sulfate)/(ammonium sulfate) is in the range, good covering power can be obtained, and a chromium plating film can be formed on an article having a complicated shape to be plated over a low current density portion.

[0017] The pH buffer used in the plating solution of the present invention is not particularly limited, examples of which include boric acid, sodium borate, potassium borate, phosphoric acid, and dipotassium hydrogen phosphate, and boric acid and sodium borate are preferred. The pH buffer may be used alone or as a combination of two or more kinds thereof. The content of the pH buffer in the plating solution of the present invention is not particularly limited, and for example, is from 30 to 150 g/L, and preferably from 50 to 110 g/L.

[0018] The sulfur-containing organic compound used in the plating solution of the present invention is a combination of saccharin or a salt thereof and a sulfur-containing organic compound having an allyl group. Examples of the saccharin or a salt thereof include saccharin and sodium saccharinate. Examples of the sulfur-containing organic compound having an allyl group include sodium allylsulfonate, allylthiourea, ammonium 2-methylallylsulfonate, and allyl isothiocyanate. The sulfur-containing organic compound having an allyl group may be used alone or as a combination of two or more kinds thereof, and sodium allylsulfonate and/or allylthiourea are preferred. Preferred examples of the combination as the sulfur-containing organic compound include sodium saccharinate and sodium allylsulfonate. The content of the sulfur-containing organic compound in the plating solution of the present invention is not particularly limited, and for example, is from 0.5 to 10 g/L, and preferably from 2 to 8 g/L.

[0019] The plating solution of the present invention may further contain ascorbic acid, sodium ascorbate, hydrogen peroxide, polyethylene glycol, and the like.

[0020] The pH of the plating solution of the present invention is not particularly limited, as far as the solution is acidic, and for example, is preferably from 2 to 4.5, and more preferably from 2.5 to 4.0.

[0021] The preparation method of the plating solution of the present invention is not particularly limited, and for example,

the solution can be prepared in such a manner that the trivalent chromium compound, the complexing agent, the conductive salt, and the pH buffer are added to water at from 40 to 50°C and dissolved therein by mixing, then the sulfur-containing organic compound is added thereto and mixed therein, and finally the pH thereof is controlled with sulfuric acid, aqueous ammonia, or the like.

[0022] Chromium plating can be formed on an article to be plated by electroplating the article to be plated with the plating solution of the present invention in the same manner as for the ordinary chromium plating solution.

[0023] The condition of the electroplating is not particularly limited, and for example, the electroplating may be performed at a bath temperature of from 30 to 60°C, with carbon or iridium oxide as an anode, at a cathode current density of from 2 to 20 A/dm², for a period of from 1 to 15 minutes.

[0024] Examples of the article to be plated capable of being electroplated include a metal, such as iron, stainless steel, and brass, and a resin, such as ABS and PC/ABS. The article to be plated may be subjected to a treatment, such as copper plating and nickel plating, in advance before the treatment with the plating solution of the present invention.

[0025] The chromium-plated product thus obtained becomes a chromium-plated product having an appearance, throwing power, and a deposition rate that are equivalent to the use of hexavalent chromium.

[0026] As another embodiment of the plating solution of the present invention, a trivalent chromium plating solution that has a high plating deposition rate, has good color tone and good corrosion resistance, and is practical is then described.

[0027] As the complexing agent of the aforementioned plating solution of the present invention, a carboxylic acid having two or more carboxy groups having a number of carbon atoms of 4 or more or a salt thereof is further used in combination, in addition to the aforementioned compound. Examples of the carboxylic acid having two or more carboxy groups having a number of carbon atoms of 4 or more or a salt thereof include a carboxylic acid, such as adipic acid, phthalic acid, pimelic acid, and sebacic acid, and a salt of the carboxylic acid. In the case where a combination of the carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof and the carboxylic acid having two or more carboxy groups having a number of carbon atoms of 4 or more or a salt thereof is used as the complexing agent, the two kinds of the complexing agents each may be used alone or as a combination of two or more kinds thereof. In the case where a combination of the carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof and the carboxylic acid having two or more carboxy groups having a number of carbon atoms of 4 or more or a salt thereof is used as the complexing agent, the total content of the complexing agents in the plating solution of the present invention is not particularly limited, and for example, is from 5 to 90 g/L, and preferably from 10 to 60 g/L, in terms of total of all the complexing agents.

[0028] As the sulfur-containing organic compound of the aforementioned plating solution of the present invention, a sulfonic acid having a vinyl group or a salt thereof may further be used in combination, in addition to the aforementioned compounds. Examples of the sulfonic acid having a vinyl group or a salt thereof include sodium vinylsulfonate, methyl vinylsulfonate, and polyvinylsulfonic acid. In the case where a combination of the saccharin or a salt thereof, the sulfonic acid having an allyl group or a salt thereof, and the sulfonic acid having a vinyl group or a salt thereof is used as the sulfur-containing organic compound, the three kinds of the sulfur-containing organic compounds each may be used alone or as a combination of two or more kinds thereof. The content of the sulfur-containing organic compounds in the plating solution of the present invention is not particularly limited, and for example, is from 0.5 to 10 g/L, and preferably from 2 to 8 g/L, in terms of total of all the sulfur-containing organic compounds.

[0029] The plating solution of the present invention that uses the complexing agents and the sulfur-containing organic compounds described above can be prepared in the preparation method described above. Chromium plating can be formed therewith on an article to be plated in the method described above.

[0030] The chromium-plated product thus obtained becomes chromium plating having a color tone that is equivalent to the use of hexavalent chromium, and having high corrosion resistance and high practicality. Accordingly, the chromium-plated product is favorably applied to components of automobiles, motorcycles, faucets, and the like, which are demanded to have corrosion resistance.

[0031] An ordinary trivalent chromium plating solution contains iron or cobalt for the enhancement of the throwing power for a low current density, but the plating solution of the present invention can have enhanced throwing power without the addition of iron and/or cobalt. A plating solution containing iron or cobalt has a tendency that the corrosion resistance of the plating film is decreased due to codeposition of iron or cobalt therein. Accordingly, it is preferred that the plating solution of the present invention contains substantially no iron and/or cobalt. The plating solution of the present invention that contains substantially no iron and/or cobalt means that the content of iron and/or cobalt is 2 ppm or less, preferably 1 ppm or less, and more preferably 0.5 ppm or less. The amount of iron and/or cobalt can be analyzed by the ICP-MS method, the atomic absorption spectrometry, or the like.

[0032] In the case where the plating solution of the present invention contains substantially no iron and/or cobalt, the resulting chromium-plated product also contains substantially no iron and/or cobalt. The chromium-plated product of the present invention that contains substantially no iron and/or cobalt means that the content of iron and/or chromium in the chromium plating is less than 0.5% by atom, and preferably 0.4% by atom or less. The amount of iron and/or cobalt can

be analyzed by EDS, XPS, or the like.

Examples

5 **[0033]** The present invention will be described in detail with reference to examples and comparative examples below, but the present invention is not limited to the examples.

Example 1

10 Chromium Plating

[0034] The components shown in Table 1 were dissolved in water to prepare a trivalent chromium plating solution. The trivalent chromium plating solution was subjected to the Hull cell test using a brass plate having nickel plating formed thereon. The condition of the Hull cell test was a current of 4 A and a plating time of 3 minutes. After plating, the distance of the deposition of the plating film from the left end of the brass plate was measured as shown in Fig. 1, and was designated as the throwing power. The film thickness at the position of the brass plate corresponding to a current density of 8 ASD was measured by the X-ray fluorescent spectrometry. The appearance after plating was evaluated in terms of the L value, the a value, and the b value with a color-difference meter (produced by Konica Minolta, Inc.). The results are shown in Table 1.

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Table 1

Composition of plating solution	Composition 1	Composition 2	Composition 3	Composition 4	Composition 5	Composition 6
Basic chromium sulfate (g/L)	64	64	64	64	64	64
Diammonium tartarate (g/L) *1	30	30	30	30	30	-
Ammonium lactate (g/L) *2	-	-	-	-	-	30
Potassium sulfate (g/L)	150	150	150	150	150	150
Ammonium sulfate (g/L)	20	20	20	20	20	20
Boric acid (g/L)	80	80	80	80	80	80
Sodium Saccharate (g/L)	4	4	4	4	4	4
Sodium allylsulfonate (36%) (ml/L)	1.58	-	-	-	-	1.58
Sodium vinylsulfonate (27.5%) (ml/L)	-	1	-	-	-	-
Sodium propinesulfonate (20%) (ml/L)	-	-	1	-	-	-
Allylthiourea (ppm)	-	-	-	10	20	-
pH of plating solution	3.4	3.4	3.4	3.4	3.4	3.4
Bath temperature (°C)	45	45	45	45	45	45
Throwing power (mm)	75	75	*	75	74	74
Film thickness (μm)	0.15	0.07	*	0.13	0.15	0.08
Appearance L value	82.38	75.47	*	82.60	82.40	80.01
Appearance a value	-0.76	-0.29	*	-0.76	-0.72	-0.75
Appearance b value	-0.42	1.94	-*	-0.22	-0.33	0.23

-: no plating deposited
 *1: two hydroxy groups and two carboxy groups
 *2: one hydroxy group and one carboxy group
 note: Hexavalent chromium plating has L value of 84, a value of -1.0, and b value of -1.0.

[0035] It was found from the results that in the case where the trivalent chromium plating solution used diammonium tartarate (having two hydroxy groups and two carboxy group) as the complexing agent, and a combination of sodium saccharate and sodium allylsulfonate or allylthiourea (i.e., the sulfur-containing organic compound having an allyl group) as the sulfur-containing organic compound (Compositions 1, 4, and 5), the appearance was equivalent to hexavalent chromium plating, and the film thickness (i.e., the deposition rate) was approximately twice the case where these compounds were not used.

[0036] The contents of iron and cobalt in the trivalent chromium plating solutions each were less than 0.5 ppm, as measured by the ICP-MS method. The contents of iron and cobalt in the resulting chromium plating each were less than 0.4% by atom, as measured by the EDS elemental analysis.

Example 2

Chromium Plating

[0037] The components shown in Table 2 were dissolved in water to prepare a trivalent chromium plating solution. The trivalent chromium plating solution was subjected to the Hull cell test using a brass plate having nickel plating formed thereon. The condition of the Hull cell test was a current of 4 A and a plating time of 3 minutes. After plating, the distance of the deposition of the plating film from the left end of the brass plate was measured. The results are shown in Table 2. The relationship between the ratio (potassium sulfate) / (ammonium sulfate) and the throwing power is shown in Fig. 2

Table 2

Composition of plating solution	Composition 7	Composition 8	Composition 9	Composition 10	Composition 11	Composition 12	Composition 13	Composition 14	Composition 15
Basic chromium sulfate (g/L)	64	64	64	64	64	64	64	64	64
Diammonium tartarate (g/L)	30	30	30	30	30	30	30	30	30
Potassium sulfate (g/L)	150	150	150	120	85	60	40	20	5
Ammonium sulfate (g/L)	20	5	40	60	85	120	150	150	150
Boric acid (g/L)	80	80	80	80	80	80	80	80	80
Sodium Saccharate (g/L)	4	4	4	4	4	4	4	4	4
Sodium allylsulfonate (36%) (m/L)	1.58	1.58	1.58	1.58	1.58	1.58	1.58	1.58	1.58
pH of plating solution	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4
Bath temperature (°C)	45	45	45	45	45	45	45	45	45
Throwing power (mm)	75	79	71	70	69	67	64	62	62

[0038] It was found that in the case where plating was performed with the aforementioned trivalent chromium plating solutions, the appearance and the film thickness were substantially the same in all the compositions, but the throwing power became better with a larger ratio (potassium sulfate)/(ammonium sulfate), and the throwing power became particularly good with the ratio of from 1.0 to 30.

[0039] The contents of iron and cobalt in the trivalent chromium plating solutions each were less than 0.5 ppm, as measured by the ICP-MS method. The contents of iron and cobalt in the resulting chromium plating each were less than 0.4% by atom, as measured by the EDS elemental analysis.

Example 3

Chromium Plating

[0040] The components shown in Table 3 were dissolved in water to prepare a trivalent chromium plating solution. The trivalent chromium plating solution was subjected to the Hull cell test using a brass plate having nickel plating formed thereon. The condition of the Hull cell test was a current of 4 A and a plating time of 3 minutes. After plating, the distance of the deposition of the plating film from the left end of the brass plate was measured as shown in Fig. 1, and was designated as the throwing power. The film thickness at the position of the brass plate corresponding to a current density of 8 ASD was measured by the X-ray fluorescent spectrometry. The appearance after plating was evaluated in terms of the L value, the a value, and the b value with a color-difference meter (produced by Konica Minolta, Inc.). The results are shown in Table 3.

Table 3

Composition of plating solution	Composition 16	Composition 17	Composition 18	Composition 19	Composition 20	Composition 21
Basicchromium sulfate (g/L)	64	64	64	64	64	64
Diammonium tartarate (g/L)	30	30	30	30	30	30
Adipic acid (g/L)	-	-	1	5	-	-
Phthalic acid (g/L)	1	5	-	-	-	-
Glycine (g/L)	-	-	-	-	-	1
Potassium sulfate (g/L)	150	150	150	150	150	150
Ammonium sulfate (g/L)	20	20	20	20	20	20
Boric acid (g/L)	80	80	80	80	80	80
Sodium Saccharate (g/L)	4	4	4	4	4	4
Sodium allylsulfonate (36%) (ml/L)	3.6	3.6	7.2	7.2	3.6	3.6
Sodium vinylsulfonate (25%) (ml/L)	3	3	5	5	3	3
pH of plating solution	3.4	3.4	3.4	3.4	3.4	3.4
Bath temperature (°C)	45	45	45	45	45	45

(continued)

Composition of plating solution	Composition 16	Composition 17	Composition 18	Composition 19	Composition 20	Composition 21
Throwing power (mm)	76	75	75	74	75	75
Film thickness (μm)	0.14	0.11	0.14	0.12	0.15	0.13
Appearance L value	82.0	81.8	82.2	82.0	82.8	81.7
Appearance a value	-0.78	-0.72	-0.77	-0.74	-0.64	-0.74
Appearance b value	-0.25	-0.10	-0.33	-0.17	-0.58	-0.14
note: Hexavalent chromium plating has L value of 84, a value of -1.0, and b value of -1.0.						

[0041] It was found from the results that in the case where the trivalent chromium plating solution used a combination of a carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof and a carboxylic acid having two or more carboxy groups having a number of carbon atoms of 4 or more or a salt thereof as the complexing agent, and a combination of saccharate or a salt thereof, a sulfonic acid having an allyl group or a salt thereof, and a sulfonic acid having a vinyl group or a salt thereof as the sulfur-containing organic compound, the appearance was equivalent to hexavalent chromium plating.

[0042] The contents of iron and cobalt in the trivalent chromium plating solutions each were less than 0.5 ppm, as measured by the ICP-MS method. The contents of iron and cobalt in the resulting chromium plating each were less than 0.4% by atom, as measured by the EDS elemental analysis.

Example 4

CASS Test

[0043] Trivalent chromium plating solutions having the compositions 16, 18, 20, and 21 shown in Table 3 were prepared. With each of the trivalent chromium plating solutions, chromium plating was formed on a copper plate having nickel plating (2 μm) thereon under condition of a bath temperature of 45°C and a current density of 8 A/dm² for 3 minutes, so as to prepare a test piece. The test piece was subjected to the CASS test (according to JIS H8502) . The micrographs of the test pieces after the CASS test for 24 hours are shown in Fig. 3.

[0044] It was found from the results of the CASS test that in the case where the trivalent chromium plating solution used a combination of a carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof and a carboxylic acid having two or more carboxy groups having a number of carbon atoms of 4 or more or a salt thereof as the complexing agent, and a combination of saccharate or a salt thereof, a sulfonic acid having an allyl group or a salt thereof, and a sulfonic acid having a vinyl group or a salt thereof as the sulfur-containing organic compound, the corrosion pores were finely dispersed to enhance the corrosion resistance.

Industrial Applicability

[0045] The trivalent chromium plating solution of the present invention can be applied to various purposes as similar to plating with hexavalent chromium.

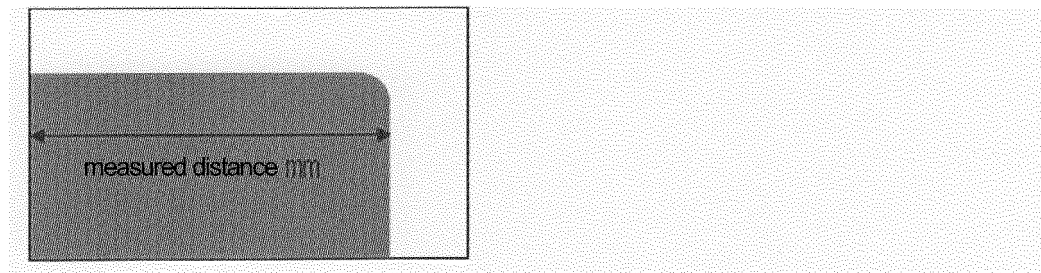
Claims

1. A trivalent chromium plating solution comprising a trivalent chromium compound, a complexing agent, potassium sulfate and ammonium sulfate as a conductive salt, a pH buffer, and a sulfur-containing organic compound, comprising a carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof as the complexing agent, and comprising a combination of saccharin or a salt thereof and a sulfur-containing organic compound having an allyl

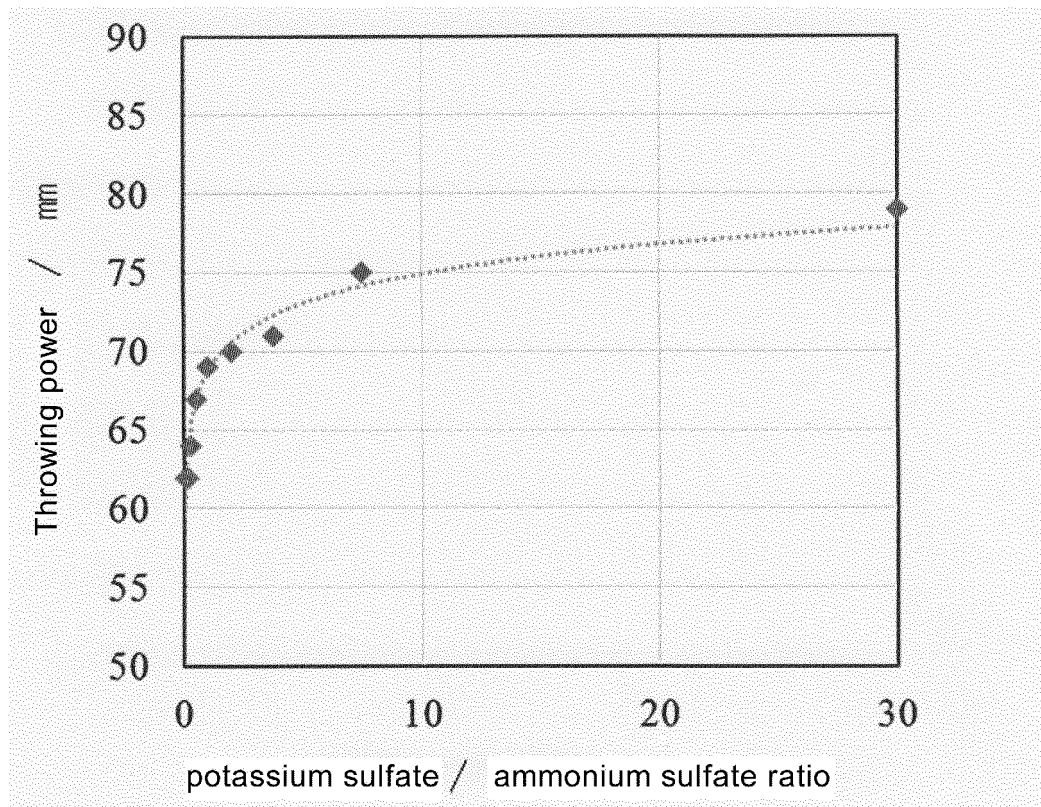
group as the sulfur-containing organic compound.

2. The trivalent chromium plating solution according to claim 1, wherein the carboxylic acid having two or more hydroxy groups or a salt thereof is diammonium tartarate.
3. The trivalent chromium plating solution according to claim 1 or 2, wherein the trivalent chromium plating solution has a mass ratio of potassium sulfate and ammonium sulfate ((potassium sulfate)/(ammonium sulfate)) of from 1.0 to 30.
4. The trivalent chromium plating solution according to any one of claims 1 to 3, wherein the sulfur-containing organic compound having an allyl group is sodium allylsulfonate and/or allylthiourea.
5. The trivalent chromium plating solution according to any one of claims 1 to 4, wherein the trivalent chromium plating solution further comprises a carboxylic acid having two or more carboxy groups having a number of carbon atoms of 4 or more or a salt thereof as the complexing agent, and a sulfonic acid having a vinyl group or a salt thereof as the sulfur-containing organic compound.
6. The trivalent chromium plating solution according to claim 5, wherein the carboxylic acid having two or more carboxy groups having a number of carbon atoms of 4 or more or a salt thereof is phthalic acid or adipic acid.
7. The trivalent chromium plating solution according to claim 5, wherein the sulfonic acid having a vinyl group or a salt thereof is sodium vinylsulfonate.
8. The trivalent chromium plating solution according to any one of claims 1 to 7, wherein the trivalent chromium plating solution comprises substantially no iron and/or cobalt.
9. A method for chromium-plating on an article to be plated, comprising electroplating an article to be plated with the trivalent chromium plating solution according to any one of claims 1 to 8.
10. A chromium-plated product comprising an article to be plated, electroplated with the trivalent chromium plating solution according to any one of claims 1 to 8.
11. The chromium-plated product according to claim 10, wherein the chromium plating contains substantially no iron and/or cobalt.

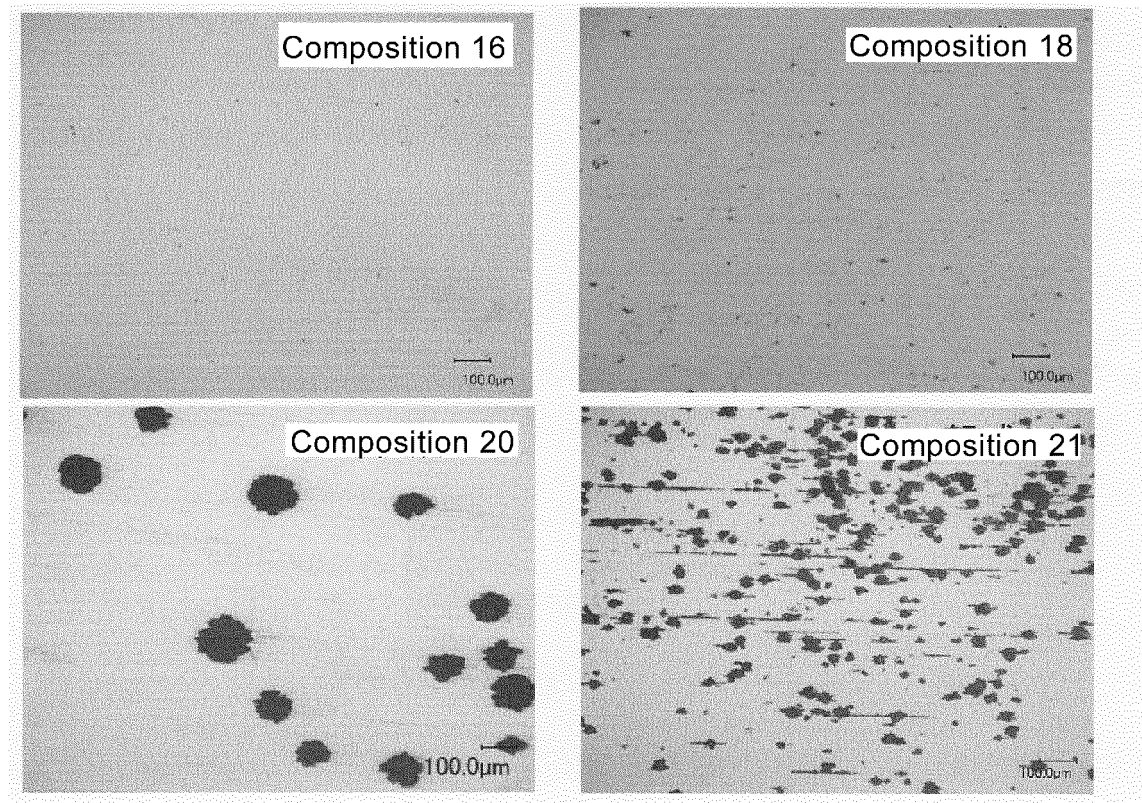
[FIG.1]



[FIG.2]



[FIG.3]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/045593

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C25D3/06 (2006.01) i

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)

Int.Cl. C25D3/06

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2019

Registered utility model specifications of Japan 1996-2019

Published registered utility model applications of Japan 1994-2019

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

CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 105671599 A (JINAN DILIGENCE TECH CO., LTD.) 15 June 2016, claims, examples 1-5 (Family: none)	1-11
A	JP 57-152483 A (W. CANNING MATERIALS LIMITED) 20 September 1982, claims, page 3, lower left column, line 18 to page 6, upper left column, line 3 & US 4473448 A, claims, column 2, line 15 to column 5, line 7 & GB 2093861 A & EP 58044 A1 & AT 20482 E & AU 8028082 A & ZA 8200769 A	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-521495 A (MACDERMID ACUMEN, INC.) 13 September 2012, claims, examples & US 2010/0243463 A1, claims, examples & WO 2010/110812 A1 & EP 2411567 A1 & TW 201035388 A & CN 102362012 A	1-11

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 5696134 B [0005]