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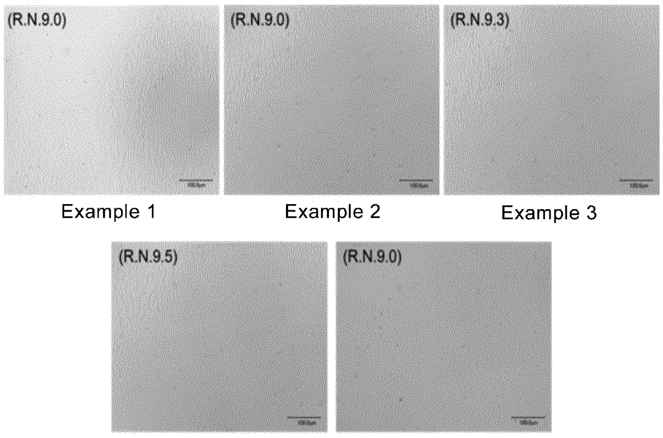
(54) TRIVALENT CHROMIUM PLATING SOLUTION AND CHROMIUM PLATING METHOD USING SAME

(57) A trivalent chromium plating solution containing a trivalent chromium compound, a complexing agent, a conductive salt, and a pH-buffering agent, and further containing an organic compound having 2-4 carbon atoms and three or more chloro groups, and a trivalent chromium plating method using the same provide a practical trivalent chromium plating with enhanced corrosion resistance as compared to the ordinary trivalent chromium plating.

[FIG.1]



Example 1 Example 2 Example 3

Example 4 Example 5

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Description

Technical Field

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

Background Art

[0002] A chromium plating has been used as a decorative coating film due to the silver-white appearance thereof. Hexavalent chromium has been used for the chromium plating, but the use of hexavalent chromium is being restricted in recent years since hexavalent chromium adversely affects the environments, and the technologies are being shifted to the use of trivalent chromium.

[0003] However, a trivalent chromium plating is inferior in corrosion resistance to a hexavalent chromium plating. Under the circumstances, the techniques for enhancing the corrosion resistance of the trivalent chromium plating have been reported. For example, PTL 1 reports the technique of the enhancement of corrosion resistance in a calcium chloride environment.

[0004] However, this trivalent chromium plating is still inferior in CASS corrosion resistance to the hexavalent chromium plating, and is not practical.

Citation List

Patent Literature

[0005] PTL 1: JP-A-2012-521495

Summary of Invention

Technical Problem

[0006] A problem of the present invention is to provide a practical trivalent chromium plating with enhanced corrosion resistance as compared to the ordinary trivalent chromium plating.

Solution to Problem

[0007] As a result of earnest investigations for solving the problem by the present inventors, it has been found that a trivalent chromium plating obtained with a trivalent chromium plating solution having added thereto an organic compound having 2-4 carbon atoms and three or more chloro groups has high corrosion resistance and is practical, and thus the present invention has been completed.

[0008] The present invention relates to a trivalent chromium plating solution containing a trivalent chromium compound, a complexing agent, a conductive salt, and a pH-buffering agent,
the trivalent chromium plating solution further containing an organic compound having 2-4 carbon atoms and three or more chloro groups .

[0009] The present invention also relates to an additive for a trivalent chromium plating solution, containing an organic compound having 2-4 carbon atoms and three or more chloro groups as an active ingredient.

[0010] The present invention further relates to a chromium plating method for an article to be plated, including electroplating the article to be plated with the trivalent chromium plating solution.

[0011] The present invention still further relates to a method for enhancing corrosion resistance of an article to be plated, including electroplating the article to be plated with the trivalent chromium plating solution.

[0012] The present invention still further relates to a chromium plated product obtained by electroplating an article to be plated with the trivalent chromium plating solution.

Advantageous Effects of Invention

[0013] The trivalent chromium plating solution of the present invention can provide a plating that has an appearance equivalent to a plating formed by using hexavalent chromium, irrespective of the use of trivalent chromium, and further has enhanced corrosion resistance and practicality.

Brief Description of Drawings

[0014]

Fig. 1 is a figure showing results of a corrosion resistance test (CASS test) performed (Examples 1 to 5).
Fig. 2 is a figure showing results of the corrosion resistance test (CASS test) performed (Comparative Examples 1 and 2 and Reference Example).
Fig. 3 is a figure showing results of the corrosion resistance test (CASS test) performed (Examples 6 to 8).

Description of Embodiments

[0015] The trivalent chromium plating solution of the present invention (hereinafter referred to as a "plating solution of the present invention") is obtained by adding an organic compound having 2-4 carbon atoms and three or more chloro groups, to a trivalent chromium plating solution containing a trivalent chromium compound, a complexing agent, a conductive salt, and a pH-buffering agent.

[0016] The organic compound having 2-4 carbon atoms and three or more chloro groups used in the plating solution of the present invention (which may be hereinafter referred simply to as an "organic compound") is not particularly limited, and examples of which include chloral hydrate, trichloroethylene, trichloroacetic acid, trichloroacetonitrile, and trichloroethanol. The organic compound may be used alone, or two or more kinds thereof may be used. Among these organic compounds, chloral hydrate and/or trichloroethylene are preferred, and chloral hydrate is more preferred. The content of the organic compound in the plating solution of the present invention is not particularly limited, and is, for example, 10 to 5,000 mg/L, preferably 20 to 2,000 mg/L, and more preferably 50 to 1,000 mg/L.

[0017] The organic compound can form an additive for a trivalent chromium plating solution using the organic compound as an active ingredient. The additive for a trivalent chromium plating solution may be added to the ordinary trivalent chromium plating solution.

[0018] 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 two or more kinds thereof may be used in combination. The content of the trivalent chromium compound in the plating solution of the present invention is not particularly limited, and is, for example, 1 to 25 g/L, and preferably 1 to 15 g/L, in terms of metallic chromium.

[0019] The complexing agent used in the plating solution of the present invention is not particularly limited, examples of which include an aliphatic monocarboxylic acid, such as formic acid, ammonium formate, and potassium formate, an aliphatic dicarboxylic acid, such as succinic acid, maleic acid, malic acid, citric acid, and triammonium citrate, and a carboxylic acid having two or more hydroxy groups and two or more carboxy groups, such as tartaric acid, diammonium tartrate, and sodium tartrate. The complexing agent may be used alone, or two or more kinds thereof may be used in combination. The content of the complexing agent in the plating solution of the present invention is not particularly limited, and is, for example, 0.1 to 50 g/L, and preferably 1 to 30 g/L.

[0020] The conductive salt used in the plating solution of the present invention is not particularly limited, examples of which include a sulfate, such as potassium sulfate, ammonium sulfate, and sodium sulfate, a chloride, such as potassium chloride, ammonium chloride, and sodium chloride, and a sulfamate, such as potassium sulfamate, ammonium sulfamate, and sodium sulfamate. These conductive salts are used as each of the groups, for example, groups of sulfates, chlorides, and the like. Among the conductive salts, a sulfate and a chloride are preferred. The conductive salt may be used alone, or two or more kinds thereof may be used in combination. The content of the conductive salt in the plating solution of the present invention is not particularly limited, and is, for example, 100 to 500 g/L, and preferably 150 to 300 g/L.

[0021] The pH-buffering agent used in the plating solution of the present invention is not particularly limited, and may be boric acid, sodium borate, potassium borate, phosphoric acid, dipotassium hydrogen phosphate, or the like. Among these, boric acid and sodium borate are preferred. The pH-buffering agent may be used alone, or two or more kinds thereof may be used in combination. The content of the pH-buffering agent in the plating solution of the present invention is not particularly limited, and is, for example, 25 to 200 g/L, and preferably 50 to 100 g/L.

[0022] The plating solution of the present invention may further contain ascorbic acid, sodium ascorbate, hydrogen peroxide, polyethylene glycol, a tin salt, such as tin sulfate and tin chloride, and the like.

[0023] The pH of the plating solution of the present invention is not particularly limited, as far as the pH is in an acidic range, and is, for example, preferably 2 to 4.5, and more preferably 2.5 to 4.0.

[0024] In the case where the conductive salt of the plating solution of the present invention is a sulfate, the complexing agent used is preferably 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 the carboxylic acid, such as tartaric acid, and the salt of the carboxylic acid, such as diammonium tartrate, Rochelle salt, and sodium tartrate. Among these complexing agents, tartaric acid and diammonium tartrate are preferred, and diammonium tartrate is more preferred. The complexing agent may be used alone, or two or more kinds thereof may be used in combination. The content of the carboxylic acid or the salt thereof in the plating solution of the present invention is not particularly limited, and is, for example, 0.1 to 90 g/L, and preferably 1 to 60 g/L. In the present invention, a hydroxy group in the carboxy group is not counted as the hydroxy group.

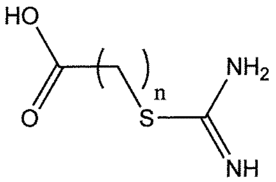
[0025] In the case where the conductive salt of the plating solution of the present invention is a sulfate, furthermore, a carboxylic acid having two or more carboxy groups and 4 or more carbon atoms or a salt thereof is preferably used in combination with the complexing agent. Examples of the carboxylic acid having two or more carboxy groups and 4 or more carbon atoms or a salt thereof include a carboxylic acid, such as adipic acid, phthalic acid, pimelic acid, and sebacic acid, and salts of the carboxylic acids. The complexing agent may be used alone, or two or more kinds thereof may be used in combination, and phthalic acid and/or adipic acid are preferred. The content of the carboxylic acid having two or more carboxy groups and 4 or more carbon atoms or a salt thereof in the plating solution of the present invention is not particularly limited, and the carboxylic acid having two or more carboxy groups and 4 or more carbon atoms or a salt thereof may be used as a part of the carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof within the range of the content thereof. The use of the carboxylic acid having two or more carboxy groups and 4 or more carbon atoms or a salt thereof enhances the corrosion resistance without a chromate treatment described later performed.

[0026] In the case where the conductive salt of the plating solution of the present invention is a sulfate, furthermore, a sulfur-containing organic compound is preferably contained. The sulfur-containing organic compound used in the plating solution of the present invention is not particularly limited, and examples of which include saccharin or a salt thereof, a sulfur-containing organic compound having an allyl group, a carboxylic acid having a carbamimidoylthio group and a dehydration reaction product thereof, thiourea, and sodium thiocyanate.

[0027] Examples of the saccharin or a salt thereof include saccharin and sodium saccharate. Among these, sodium saccharate is preferred.

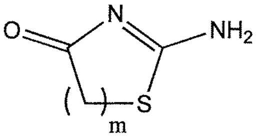
[0028] Examples of the sulfur-containing organic compound having an allyl group include sodium allylsulfonate, allylthiourea, ammonium 2-methylallylsulfonate, and allyl isothiocyanate. Among these, sodium allylsulfonate and/or allylthiourea are preferred.

[0029] Examples of the carboxylic acid having a carbamimidoylthio group and a dehydration reaction product thereof include a carboxylic acid having a carbamimidoylthio group represented by the general formula (1) and a dehydration reaction product of a carboxylic acid having a carbamimidoylthio group represented by the general formula (2).



(1)

In the formula (1), n represents an integer of 1 to 5, preferably 1 to 2.



(2)

[0030] In the formula (2), m represents an integer of 1 or 2.

[0031] Specific examples of the carboxylic acid having a carbamimidoylthio group and a dehydration reaction product thereof include [[amino(imino)methyl]thio]acetic acid, 3-[[amino(imino)methyl]thio]propanoic acid, 2-iminothiazolidin-4-one, and 2-amino-5,6-dihydro-4H-1,3-thiazin-4-one.

[0032] The sulfur-containing organic compound may be used alone, or two or more kinds thereof may be used in combination. Among the sulfur-containing organic compounds, a combination of saccharin or a salt thereof and one or more kind selected from the group consisting of a sulfur-containing organic compound having an allyl group and a carboxylic acid having a carbamimidoylthio group and/or a dehydration reaction product thereof is preferred, and a combination of sodium saccharate and sodium allylsulfonate is particularly preferred. The content of the sulfur-containing organic compound in the plating solution of the present invention is not particularly limited, and is, for example, 0.5 to 10 g/L, and preferably 2 to 8 g/L.

[0033] In the case where the conductive salt of the plating solution of the present invention is a sulfate, it is particularly preferred that a carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof is used as the complexing agent, and a combination of saccharin or a salt thereof and one or more kind selected from the group consisting of a sulfur-containing organic compound having an allyl group and a carboxylic acid having a carbamimidoylthio group and/or a dehydration reaction product thereof is used as the sulfur-containing organic compound.

[0034] The preparation method of the plating solution of the present invention described above is not particularly limited, and the plating solution may be prepared, for example, in such a manner that the trivalent chromium compound, the complexing agent, the conductive salt, and the pH-buffering agent are added to water at 40 to 60°C and mixed and dissolved therein, then the organic compound having 2-4 carbon atoms and three or more chloro groups and depending on necessity the sulfur-containing organic compound are added thereto and mixed therein, and finally the pH is regulated with sulfuric acid, aqueous ammonia, or the like.

[0035] The plating solution of the present invention can provide a chromium plating on an article to be plated by electroplating the article to be plated with the plating solution of the present invention, similarly to the ordinary chromium plating solution. Further, corrosion resistance is enhanced by the electroplating.

[0036] The condition of the electroplating is not particularly limited, and the electroplating may be performed, for example, at a bath temperature of 30 to 60°C, with an anode formed of carbon or iridium oxide, at a cathode current density of 2 to 20 A/dm^2, for 1 to 15 minutes.

[0037] 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.

[0038] In the case where the article to be plated is subjected to a nickel plating three layers or four layers of nickel plating layers are preferably provided by the ordinary method. In the case of three layers, a semibright nickel plating, a bright nickel plating, and a microporous nickel plating may be provided in this order. In this case, the potential differences among the layers are not particularly limited, and for example, it is preferred that the potential difference of the bright nickel plating is - 200 to -60 mV with respect to the semibright nickel plating, and the potential difference of the microporous nickel plating is 20 to 100 mV with respect to the bright nickel plating. In the case of four layers, a semibright nickel plating, a high sulfur content nickel plating, a bright nickel plating, and a microporous nickel plating may be provided in this order. In this case, the potential differences among the layers are not particularly limited, and for example, it is preferred that the potential difference of the bright nickel plating is - 200 to -60 mV with respect to the semibright nickel plating, the potential difference of the high sulfur content nickel plating is -50 to -5 mV with respect to the bright nickel plating, and the potential difference of the microporous nickel plating is 20 to 100 mV with respect to the bright nickel plating.

[0039] The chromium plated product thus obtained has enhanced corrosion resistance. The enhancement of the corrosion resistance herein means that the rating number (R. N.) is enhanced in the evaluation according to JIS H8502.

[0040] The chromium plating may be further subjected to a chromate treatment, and thereby the corrosion resistance is further enhanced.

[0041] The condition of the chromate treatment is not particularly limited, and for example, electroplating may be performed at a bath temperature of 25 to 70°C, with an insoluble anode, such as a lead-tin alloy, as an anode, at a cathode current density of 0.1 to 1 A/dm^2, for 1 minute.

Examples

[0042] The present invention will be described in detail with reference to examples below, but the present invention is not limited to the examples.

Examples 1 to 5

Trivalent Chromium Plating

[0043] The trivalent chromium compound, the complexing agent, the conductive salt, and the pH-buffering agent shown in Table 1 were added to water at 60°C and mixed and dissolved therein, then the organic compound having 2-4 carbon atoms and three or more chloro groups and the sulfur-containing organic compound were added thereto and mixed therein, and finally the pH was regulated with sulfuric acid, aqueous ammonia, or the like, thereby preparing a trivalent chromium plating solution. A chromium plating was formed on an article of an ABS resin having formed thereon a copper plating ("CU-BRITE EP-30", produced by JCU Corporation), a semibright nickel plating ("CF-24T", produced by JCU Corporation), a bright nickel plating ("HI-BRITE #88", produced by JCU Corporation), and a microporous nickel plating ("MP-NI 308", produced by JCU Corporation) under condition of the bath temperature shown in Table 1 and a current density of 10 A/dm^2 for 3 minutes, so as to provide a test piece. The test piece was subjected to a CASS test (JIS H8502). The micrographs of the test pieces after the CASS test for 80 hours are shown in Figs. 1 and 2. The rating numbers (R. N.) shown in the figures are evaluation in terms of total corrosion rate. The chromate treatment was performed with "EBACHRO-500", produced by JCU Corporation, under condition of a bath temperature of 40°C and a cathode current density of 0.2 A/dm^2 for 1 minute.

Table 1

Composition of plating solution	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1	Comparative Example 2	Reference Example
Basic chromium sulfate g/L	64	64	64	64	64	64	64	-
Chromium anhydride g/L	-	-	-	-	-	-	-	250
Sulfuric acid (98%) g/L	-	-	-	-	-	-	-	2.5
Malic acid g/L	15	-	-	-	-	15	-	-
Diammonium tartrate g/L	-	30	30	30	30	-	30	-
Adipic acid g/L	-	-	-	1	-	-	-	-
Sodium sulfate g/L	35	-	-	-	-	35	-	-
Potassium sulfate g/L	140	150	150	150	150	-	150	-
Ammonium sulfate g/L	30	20	20	20	20	30	20	-
Boric acid g/L	90	80	80	80	80	90	80	-
Sodium saccharate g/L	2.5	4	4	4	4	2.5	4	-
Thiourea mg/L	10	-	-	-	-	10	-	-
Sodium allylsulfonate (36%) mL/L	-	2	2	2	2	-	2	-
Chloral hydrate (810 g/L) mL/L	0.1	0.1	0.1	0.1	-	-	-	-
Trichloroethylene mL/L	-	-	-	-	26	-	-	-
pH of plating solution	3.4	3.4	3.4	3.4	3.4	3.4	3.4	-
Bath temperature °C	60	55	55	55	55	60	45	40
Chromate treatment	no	no	yes	no	no	no	yes	-

[0044] It was understood from the results of the CASS test that the addition of the organic compound having 2-4 carbon atoms and three or more chloro groups to the trivalent chromium plating solution enhanced the corrosion resistance. Some of the plating solutions of the present invention provided a high corrosion resistant film without the chromate treatment performed.

Examples 6 to 8

Trivalent Chromium Plating

[0045] The trivalent chromium compound, the complexing agent, the conductive salt, and the pH-buffering agent shown in Table 2 were added to water at 60°C and mixed and dissolved therein, then the organic compound having 2-4 carbon atoms and three or more chloro groups and the sulfur-containing organic compound were added thereto and mixed therein, and finally the pH was regulated with sulfuric acid, aqueous ammonia, or the like, thereby preparing a trivalent chromium plating solution. A chromium plating was formed on an article of an ABS resin having formed thereon a copper plating ("CU-BRITE EP-30", produced by JCU Corporation), a semibright nickel plating ("CF-24T", produced by JCU Corporation), a bright nickel plating ("HI-BRITE #88", produced by JCU Corporation), and a microporous nickel plating ("MP-NI 308", produced by JCU Corporation) under condition of the bath temperature shown in Table 2 and a current density of 10 A/dm^2 for 3 minutes, so as to provide a test piece. The test piece was subjected to a CASS test (JIS H8502). The micrographs of the test pieces after the CASS test for 80 hours are shown in Fig. 3. The rating numbers (R. N.) shown in the figure are evaluation in terms of total corrosion rate. The results are also shown in Table 2.

Table 2

Composition of plating solution	Example 6	Example 7	Example 8	Comparative Example 3
Basic chromium sulfate g/L	19.5	19.5	19.5	19.5
Diammonium tartrate g/L	3	3	3	3
Potassium sulfate g/L	150	150	150	150
Boric acid g/L	70	70	70	70
Sodium saccharate g/L	3	3	3	3
[[amino(imino)methyl]thio]acetic acid mg/L	50	-	20	50
2-Iminothiazolidin-4-one mg/L	-	50	30	-
Chloral hydrate (810 g/L) mL/L	0.25	0.25	0.25	-
pH of plating solution	3.7	3.7	3.7	3.7
Bath temperature °C	55	55	55	55
Chromate treatment	no	no	no	no
Rating number (R. N.)	9	9	9	8

[0046] It was understood from the results of the CASS test that the corrosion pitting was smaller in Example 6 than in Comparative Example 3. The similar result was obtained in Examples 7 and 8. It was understood therefrom that the addition of the organic compound having 2-4 carbon atoms and three or more chloro groups to the trivalent chromium plating solution enhanced the corrosion resistance.

Example 9

Trivalent Chromium Plating Bath

[0047] The trivalent chromium compound, the complexing agent, the conductive salt, and the pH-buffering agent shown in the following compositions 1 to 3 were added to water at 50°C and mixed and dissolved therein, then the organic compound having 2-4 carbon atoms and three or more chloro groups was added thereto and mixed therein, and finally the pH was regulated with hydrochloric acid, aqueous ammonia, or the like, thereby preparing a trivalent chromium plating solution.

<Composition 1>

Basic chromium sulfate	64 g/L
Ammonium formate	16 g/L
Potassium chloride	165 g/L
Ammonium chloride	100 g/L
Ammonium bromide	6 g/L
Boric acid	67 g/L
Chloral hydrate (810 g/L)	0.1 mL/L

<Composition 2>

[0048]

Basic chromium sulfate	64 g/L
Ammonium formate	16 g/L
Sodium chloride	75 g/L
Potassium chloride	165 g/L
Ammonium chloride	100 g/L
Ammonium bromide	6 g/L
Boric acid	67 g/L
Chloral hydrate (810 g/L)	0.1 mL/L

[0049] <Composition 3>

Basic chromium sulfate	64 g/L
Ammonium tartrate	30 g/L
Potassium sulfate	150 g/L
Ammonium sulfate	20 g/L
Boric acid	80 g/L
Chloral hydrate (810 g/L)	0.1 mL/L

Examples 10 and 11

Trivalent Chromium Plating

[0050] The trivalent chromium compound, the complexing agent, the conductive salt, and the pH-buffering agent shown in Table 3 were added to water at 60°C and mixed and dissolved therein, then the organic compound having 2-4 carbon atoms and three or more chloro groups was added thereto and mixed therein, and finally the pH was regulated with hydrochloric acid or aqueous ammonia, thereby preparing a trivalent chromium plating solution. A chromium plating was formed on an article of an ABS resin having formed thereon a copper plating ("CU-BRITE EP-30", produced by JCU Corporation), a semibright nickel plating ("CF-24T", produced by JCU Corporation), a bright nickel plating ("HI-BRITE #88", produced by JCU Corporation), and a microporous nickel plating ("MP-NI 308", produced by JCU Corporation) under condition of the bath temperature shown in Table 3 and a current density of 10 A/dm^2 for 3 minutes, so as to provide a test piece. The test piece was subjected to a CASS test (JIS H8502) . The rating numbers (R. N.) after the CASS test for 80 hours are evaluation in terms of total corrosion rate. The results are also shown in Table 3. The chromate treatment was performed with "EBACHRO-500", produced by JCU Corporation, under condition of a bath temperature of 40°C and a cathode current density of 0.2 A/dm^2 for 1 minute.

Table 3

Composition of plating solution	Example 10	Example 11	Comparative Example 4	Comparative Example 5
Basic chromium sulfate g/L	64	64	64	64
Ammonium formate g/L	16	16	16	16

(continued)

Composition of plating solution	Example 10	Example 11	Comparative Example 4	Comparative Example 5
Sodium chloride g/L	70	70	70	70
Potassium chloride g/L	140	140	140	140
Ammonium chloride g/L	85	85	85	85
Ammonium bromide g/L	6	6	6	6
Boric acid g/L	67	67	67	67
Chloral hydrate (810 g/L) mL/L	0.8	0.8	-	-
pH of plating solution	2.7	2.7	2.7	2.7
Bath temperature °C	32	32	32	32
Chromate treatment	no	yes	no	yes
Rating number (R. N.)	9	9.3	8	9

[0051] It was understood from the results of the CASS test that the addition of the organic compound having 2-4 carbon atoms and three or more chloro groups to the trivalent chromium plating solution enhanced the corrosion resistance.

Industrial Applicability

[0052] The trivalent chromium plating solution of the present invention can be applied to various purposes similarly to a plating using hexavalent chromium.

Claims

1. A trivalent chromium plating solution comprising a trivalent chromium compound, a complexing agent, a conductive salt, and a pH-buffering agent,
   the trivalent chromium plating solution further comprising an organic compound having 2-4 carbon atoms and three or more chloro groups .

2. The trivalent chromium plating solution according to claim 1, wherein the organic compound having 2-4 carbon atoms and three or more chloro groups is chloral hydrate and/or trichloroethylene.

3. The trivalent chromium plating solution according to claim 1 or 2, wherein the conductive salt is a sulfate.

4. The trivalent chromium plating solution according to claim 3, further comprising a sulfur-containing organic compound.

5. The trivalent chromium plating solution according to claim 3, wherein
   the conductive salt is a sulfate,
   the complexing agent is a carboxylic acid having two or more hydroxy groups and two or more carboxy groups or a salt thereof, and
   the sulfur-containing organic compound is a combination of saccharin or a salt thereof and
   one or more kind selected from the group consisting of a sulfur-containing organic compound having an allyl group and a carboxylic acid having a carbamimidoylthio group and/or a dehydration reaction product thereof.

6. The trivalent chromium plating solution according to claim 5, wherein the carboxylic acid having two or more hydroxy groups or a salt thereof is tartaric acid or diammonium tartrate.

7. The trivalent chromium plating solution according to claim 5 or 6, wherein the sulfur-containing organic compound having an allyl group is sodium allylsulfonate and/or allylthiourea.

8. The trivalent chromium plating solution according to any one of claims 5 to 7, further comprising a carboxylic acid having two or more carboxy groups and 4 or more carbon atoms or a salt thereof as the complexing agent.

9. The trivalent chromium plating solution according to claim 8, wherein the carboxylic acid having two or more carboxy groups and 4 or more carbon atoms or a salt thereof is phthalic acid and/or adipic acid.

10. The trivalent chromium plating solution according to claim 1 or 2, wherein the conductive salt is a chloride.

11. An additive for a trivalent chromium plating solution, comprising an organic compound having 2-4 carbon atoms and three or more chloro groups as an active ingredient.

12. A chromium plating method for an article to be plated, comprising electroplating the article to be plated with the trivalent chromium plating solution according to any one of claims 1 to 10.

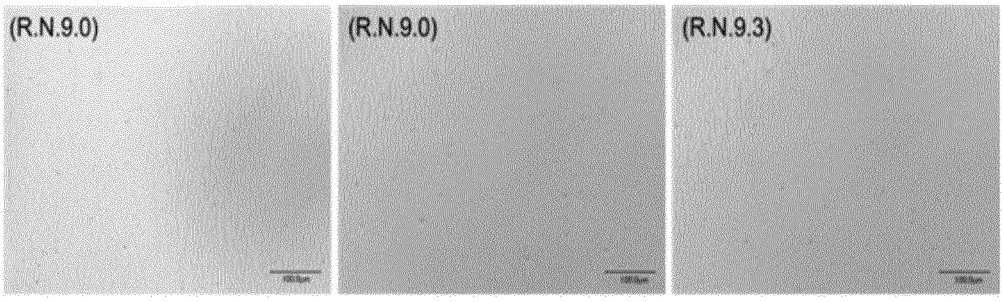
13. The chromium plating method for an article to be plated according to claim 12, further comprising performing a chromate treatment, after electroplating the article to be plated.

14. A method for enhancing corrosion resistance of an article to be plated, comprising electroplating the article to be plated with the trivalent chromium plating solution according to any one of claims 1 to 10.

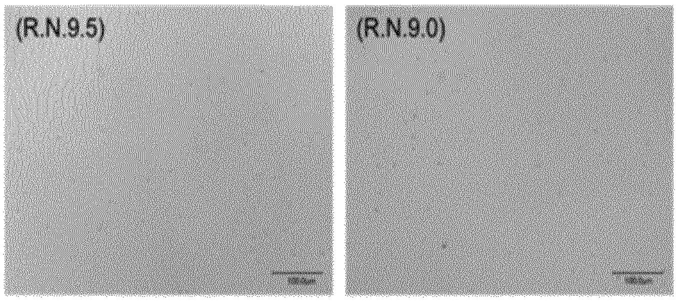
15. The method for enhancing corrosion resistance of an article to be plated according to claim 14, further comprising performing a chromate treatment, after electroplating the article to be plated.

16. A chromium plated product obtained by electroplating an article to be plated with the trivalent chromium plating solution according to any one of claims 1 to 10.

[FIG.1]

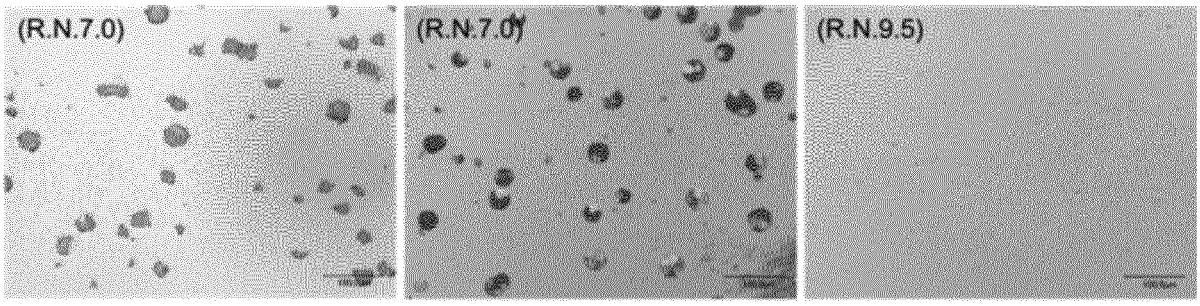


Example 1 Example 2 Example 3



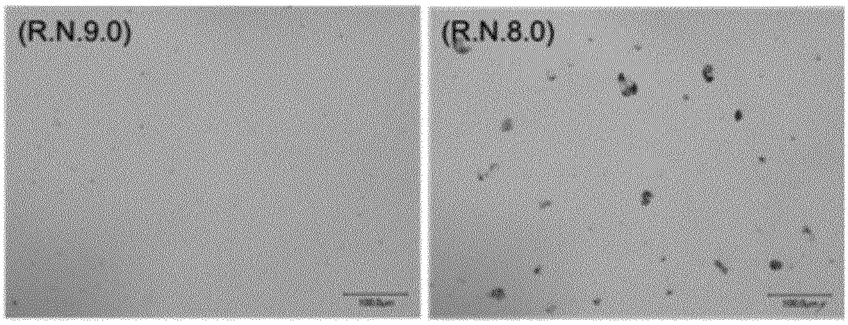
Example 4 Example 5

[FIG.2]



Comparative Example 1 Comparative Example 2 Reference Example

[FIG.3]



Example 6 Comparative Example 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/026246

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C25D3/06(2006.01)i, C25D3/10(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, C25D3/10

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 58-39791 A (M & T CHEMICALS, INC.) 08 March 1983 & US 4472249 A1 & EP 73568 A1	1-16
A	JP 2015-221944 A (NISSAN MOTOR CO., LTD.) 10 December 2015, paragraphs [0031], [0048] (Family: none)	1-16
A	JP 1-100291 A (JAPAN CARLIT CO., LTD.) 18 April 1989 (Family: none)	1-16
A	JP 2016-27211 A (ATOTECH DEUTSCHLAND GMBH) 18 February 2016, claims & WO 2014/180595 A1, claims & EP 2801640 A1	1-16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search
20 August 2019 (20.08.2019)

Date of mailing of the international search report
03 September 2019 (03.09.2019)

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2012521495 A **[0005]**