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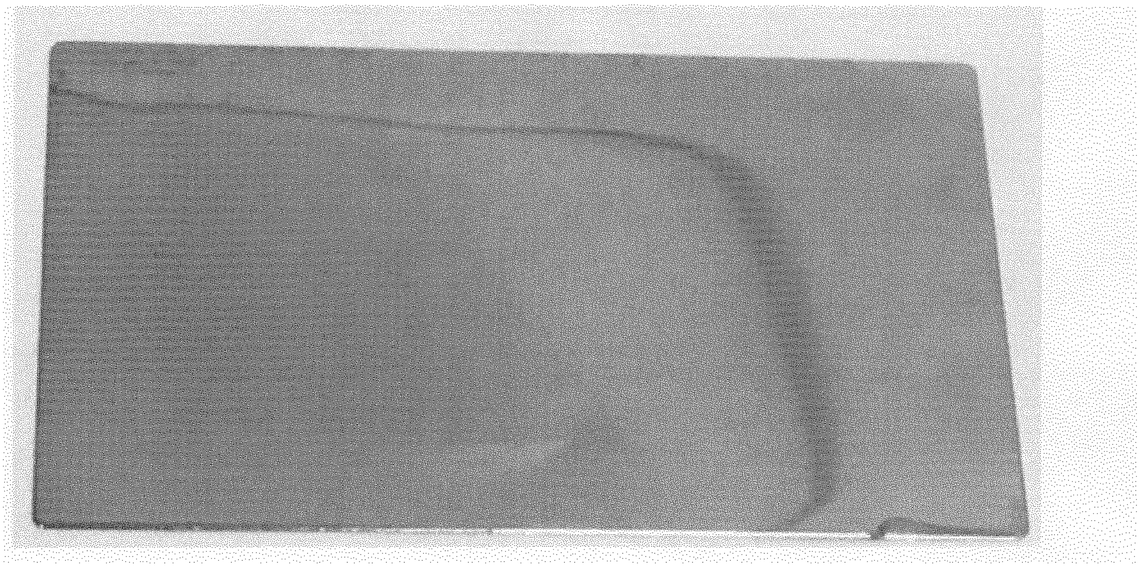
(54) TRIVALENT CHROMIUM PLATING SOLUTION AND TRIVALENT CHROMIUM PLATING METHOD USING SAME

(57) A trivalent chromium plating solution that does not cause the problems including the occurrence of deposition failure of the plating and color unevenness, such as a brown stripe pattern, in the plating even though a metal impurity is incorporated into the plating solution, and a trivalent chromium plating method are provided by a trivalent chromium plating solution containing a trivalent chromium compound, a chloride as a conductive salt, a pH buffering agent, and a complexing agent, further containing an unsaturated sulfonic acid compound represented by the following general formula (1) (wherein in the formula (1), R_1 represents a hydrocarbon group having a number of carbon atoms of from 1 to 10, hydrogen, or a halogen; R_2 represents nothing or a hydrocarbon group having a number of carbon atoms of from 1 to 10; and X represents hydrogen or an alkali metal), and a trivalent chromium plating method using the same.

$$R_1\text{-CH=CH-}R_2\text{-SO}_3X \qquad (1)$$

(Cont. next page)

[FIG.3]



Description

Technical Field

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

Background Art

[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 by various manufacturers (see, for example, PTL 1).

[0004] However, the trivalent chromium plating solution has problems including the occurrence of deposition failure of the plating and color unevenness, such as a brown stripe pattern, in the plating caused by the incorporation of metal impurities derived from the first plating and the chemicals and the like associated with the plating.

Citation List

Patent Literature

[0005] PTL 1: JP-A-2009-74170

Summary of Invention

Technical Problem

[0006] An object of the present invention is to provide a trivalent chromium plating solution that does not cause the problems including the occurrence of deposition failure of the plating and color unevenness, such as a brown stripe pattern, in the plating even though metal impurities are incorporated into the plating solution.

Solution to Problem

[0007] As a result of the earnest investigations by the present inventors, it has been found that the problems including the occurrence of deposition failure of the plating and color unevenness, such as a brown stripe pattern, in the plating can be prevented from occurring even through metal impurities are incorporated into the plating solution, by using an unsaturated sulfonic acid compound having a particular structure contained in a trivalent chromium plating solution containing a chloride as a conductive salt, and thus the present invention has been completed. Furthermore, it has also been found that not only the aforementioned problems, but also burnt deposit in a high current density in plating can be prevented from occurring, by positively using nickel as a metal impurity contained in the trivalent chromium plating solution, and thus the present invention has been completed.

[0008] Accordingly, the present invention relates to a trivalent chromium plating solution containing a trivalent chromium compound, a chloride as a conductive salt, a pH buffering agent, and a complexing agent,
further containing an unsaturated sulfonic acid compound represented by the following general formula (1):

$$R_1\text{-}CH{=}CH\text{-}R_2\text{-}SO_3X \qquad (1)$$

wherein in the formula (1), R_1 represents a hydrocarbon group having a number of carbon atoms of from 1 to 10, hydrogen, or a halogen; R_2 represents nothing or a hydrocarbon group having a number of carbon atoms of from 1 to 10; and X represents hydrogen or an alkali metal.

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

[0010] The present invention further relates to a method for enhancing resistance of a trivalent chromium plating solution containing a trivalent chromium compound, a chloride as a conductive salt, a pH buffering agent, and a complexing agent, against metal impurities contained, including using an unsaturated sulfonic acid compound represented by the following general formula (1):

R_1-CH=CH-R_2-SO_3X (1)

wherein in the formula (1), R_1 represents a hydrocarbon group having a number of carbon atoms of from 1 to 10, hydrogen, or a halogen; R_2 represents nothing or a hydrocarbon group having a number of carbon atoms of from 1 to 10; and X represents hydrogen or an alkali metal, further contained in the trivalent chromium plating solution.

[0011] The present invention still further relates to a method for preventing burnt deposit in a high current density in plating with a trivalent chromium plating solution containing a trivalent chromium compound, a chloride as a conductive salt, a pH buffering agent, and a complexing agent, including using an unsaturated sulfonic acid compound represented by the following general formula (1), and nickel:

R_1-CH=CH-R_2-SO_3X (1)

wherein in the formula (1), R_1 represents a hydrocarbon group having a number of carbon atoms of from 1 to 10, hydrogen, or a halogen; R_2 represents nothing or a hydrocarbon group having a number of carbon atoms of from 1 to 10; and X represents hydrogen or an alkali metal, further contained in the trivalent chromium plating solution.

[0012] The present invention still more further relates to a chromium-plated product including an article to be plated, electroplated with the trivalent chromium plating solution.

Advantageous Effects of Invention

[0013] The trivalent chromium plating solution of the present invention is an excellent one that does not cause the problems including the occurrence of deposition failure of the plating and color unevenness, such as a brown stripe pattern, in the plating even through metal impurities are incorporated into the plating solution.

[0014] Furthermore, not only the aforementioned problems, but also burnt deposit in a high current density in plating can be prevented from occurring by positively using nickel as a metal impurity contained in the trivalent chromium plating solution of the present invention.

Brief Description of Drawings

[0015]

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 an image showing the Hull cell appearance of the nickel-plated brass plate (with burnt deposit) after plating with the plating solution having no nickel added in Example 4.

Fig. 3 is an image showing the Hull cell appearance of the nickel-plated brass plate (without burnt deposit) after plating with the plating solution having 10 ppm of nickel added in Example 4.

Description of Embodiments

[0016] 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 chloride as a conductive salt, a pH buffering agent, and a complexing agent, and further contains an unsaturated sulfonic acid compound represented by the following general formula (1) .

R_1-CH=CH-R_2-SO_3X (1)

[0017] In the formula (1), R_1 represents a hydrocarbon group having a number of carbon atoms of from 1 to 10, hydrogen, or a halogen; R_2 represents nothing or a hydrocarbon group having a number of carbon atoms of from 1 to 10; and X represents hydrogen or an alkali metal, and it is preferred that R_1 represents a hydrocarbon group having a number of carbon atoms of from 1 to 6 or hydrogen; R_2 represents nothing or a hydrocarbon group having a number of carbon atoms of from 1 to 6; and X represents hydrogen, sodium, or potassium. Specific examples of the unsaturated sulfonic acid compound represented by the formula (1) include sodium vinylsulfonate, sodium allylsulfonate, sodium p-styrenesulfonate, and sodium β-styrenesulfonate. The unsaturated sulfonic acid compound may be used alone or as a combination of two or more kinds thereof. The content of the unsaturated sulfonic acid compound in the plating solution of the present invention is not particularly limited, and for example, is from 0.01 to 20 g/L, and preferably from 0.1 to 5 g/L.

[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, chromium sulfate, and chromium chloride 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 20 g/L, and preferably from 5 to 15 g/L, in terms of metallic chromium.

[0019] The conductive salt used in the plating solution of the present invention is a chloride. The kind of the chloride is not particularly limited, examples of which include potassium chloride, ammonium chloride, and sodium chloride. The chloride may be used alone or as a combination of two or more kinds thereof. The content of the chloride in the plating solution of the present invention is not particularly limited, and for example, is from 150 to 400 g/L, and preferably from 200 to 350 g/L.

[0020] The pH buffering agent 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 buffering agent may be used alone or as a combination of two or more kinds thereof. The content of the pH buffering agent in the plating solution of the present invention is not particularly limited, and for example, is from 10 to 150 g/L, and preferably from 50 to 100 g/L.

[0021] The complexing agent used in the plating solution of the present invention is not particularly limited, examples of which include formic acid, ammonium formate, potassium formate, citric acid, and triammonium citrate. Among these, ammonium formate and triammonium citrate are preferred. The complexing agent may be used alone or as a combination of two or more kinds thereof. The content of the complexing agent in the plating solution of the present invention is not particularly limited, and for example, is from 0.3 to 2 times by mol, and preferably from 0.8 to 1.5 times by mol, the metallic chromium concentration.

[0022] The plating solution of the present invention may further contain ammonium bromide, potassium bromide, and the like.

[0023] 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, and more preferably from 2.5 to 3.5.

[0024] The preparation method of the plating solution of the present invention is not particularly limited, and for example, the solution can be prepared by adding and mixing the trivalent chromium compound, the chloride salt, the pH buffering agent, the complexing agent, and the unsaturated sulfonic acid compound with water at from 40 to 50°C, adding and mixing the other components therewith depending on necessity, and controlling the pH thereof.

[0025] The plating solution of the present invention does not cause the problems including the occurrence of deposition failure of the plating and color unevenness, such as a brown stripe pattern, in the plating even though metal impurities are contained therein (i.e., has resistance against metal impurities). In particular, the plating solution of the present invention does not cause the problems even though a large amount of metal impurities are contained in a concentration of approximately several hundred ppm during the long-term use or suddenly. The metal impurities herein are metals derived from the first plating and the chemicals and the like associated with the plating. Specific examples of the metals include nickel, zinc, copper, and hexavalent chromium, and preferably include nickel and copper, which are frequently used as the first plating.

[0026] In the case where the plating solution of the present invention positively uses nickel as a metal impurity contained therein, burnt deposit in a high current density in plating can be prevented from occurring. The high current density herein means portions where the current is concentrated, such as a corner part and an apex part of an article. Nickel that can be used in the plating solution of the present invention is not particularly limited, and examples thereof include a nickel salt, such as nickel chloride and nickel sulfate. The content of nickel in the plating solution of the present invention is not particularly limited, and for example, is from 10 to 500 ppm, preferably from 15 to 200 ppm, and more preferably from 20 to 100 ppm.

[0027] Nickel can prevent burnt deposit in a high current density from occurring also in plating with a trivalent chromium plating solution containing a trivalent chromium compound, a chloride as a conductive salt, a pH buffering agent, and a complexing agent, obtained by excluding the unsaturated sulfonic acid compound represented by the general formula (1) from the plating solution of the present invention, at the same concentration. The kinds and the concentrations of the trivalent chromium compound, the chloride, the pH buffering agent, and the complexing agent may be the same as in the plating solution of the present invention.

[0028] 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.

[0029] 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.

[0030] The condition of the electroplating is not particularly limited, and for example, the electroplating may be performed at a bath temperature of from 25 to 45°C, with carbon or iridium oxide as an anode, at a cathode current density of from 4 to 20 A/dm^2, for a period of from 1 to 15 minutes.

[0031] 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.

[0032] The chromium plating thus obtained becomes chromium plating having an appearance, throwing power, and a deposition rate that are equivalent to the use of hexavalent chromium. The unsaturated sulfonic acid compound represented by the formula (1) can suppress the color tone of the resulting chromium plating from becoming dark, as compared to other unsaturated sulfonic acid compounds. Accordingly, the chromium-plated product is favorably applied to automobile exterior components, such as a door handle and an emblem, and components of an accessory, a faucet, a tool, and the like.

[0033] 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 0.3% by atom or less. The amount of iron and/or cobalt can be analyzed by EDS, XPS, or the like.

Examples

[0034] 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

Chromium Plating

[0035] The compounds shown in the following basic formulation and Table 1 each 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 5 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 the throwing power decreasing rate was calculated in the manner described later. The color tone and the appearance were evaluated in the manners described later. The color tone after plating was evaluated in terms of the L* value with a color-difference meter (produced by Konica Minolta, Inc.). The results are shown in Table 1.

<Basic Formulation 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

<Basic Formulation 2>

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

<Basic Formulation 3>

Basic chromium sulfate	64 g/L
Ammonium tartarate	30 g/L
Potassium sulfate	150 g/L
Ammonium sulfate	20 g/L
Boric acid	80 g/L

Table 1

	Basic formulation	Compound	Addition concentration	L*	Evaluation of color tone	Evaluation of appearance	Throwing power decreasing rate (%)
Example product	1	Na vinylsulfonate 25% aqueous solution	1 mL/L	79.54	good	good	0.70
	1	Na vinylsulfonate 25% aqueous solution	5 mL/L	79.52	good	good	1.41
	1	Na allylsulfonate 36% aqueous solution	0.5 mL/L	78.39	good	good	not decreased
	1	Na p-styrenesulfonate	1.5 g/L	79.23	good	good	not decreased
	2	Na β-styrenesulfonate	1.0 g/L	79.61	good	good	0.70
	2	Na vinylsulfonate 25% aqueous solution	1 mL/L	79.48	good	good	not decreased
Comparative product	1	not added	-	78.63	good	good	0 (standard)
	1	Na 2-propine-1-sulfonate 20% aqueous solution	0.1 mL/L	73.69	poor	good	11.27
	1	thiodiglycolic acid	1.0 g/L	76.77	poor	good	5.63
	1	thiourea	30 mg/L	75.70	poor	good	7.75
	1	1-allyl-2-thiourea	50 mg/L	75.60	poor	good	1.41
	1	Na 3-mercapto-1-propanesulfonate	50 mg/L	77.22	poor	good	2.11
	1	Na 2-hydroxyethanesulfonate 20% aqueous solution	20 mL/L	79.04	good	good	1.41
	1	Na saccharate dihydrate	50 mg/L	77.66	poor	good	1.41
	2	not added	-	78.87	good	good	0 (standard)
	3	not added	-	79.68	good	good	0 (standard)
	3	Na allylsulfonate 36% aqueous solution	1.5 mL/L	80.38	good	good	not decreased
	3	Na vinylsulfonate 25% aqueous solution	1.0 mL/L	73.47	poor	good	not decreased

<Calculation Method of Throwing Power Decreasing Rate>

[0036]

$$(\text{decreasing rate } (\%)) = ((\text{standard value} - \text{test value}))/(\text{standard value}) \times 100$$

[0037] In the expression, the standard value is a value of throwing power with no compound added, and the test value is the measured value in the test under the condition. The values of the standard value are 71 mm for the basic formulation 1, 73 mm for the basic formulation 2, and 74 mm for the basic formulation 3.

<Evaluation of Color Tone>

(Evaluation) (Content)

[0038] good: L* of 78 or more
poor: L* of less than 78

<Evaluation of Appearance>

[0039] good: uniform appearance and no uneven pattern
poor: uneven appearance or uneven pattern

[0040] It was found from the results that the unsaturated sulfonic acid compound contained in the plating solution of the present invention was not a substance that the use thereof deteriorated the color tone, the appearance, and the throwing power of the chromium plating.

[0041] 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 0.3% by atom, as measured by the EDS elemental analysis.

Example 2

Chromium Plating in presence of Impurity

[0042] A trivalent chromium plating solution was prepared in the same manner as in Example 1 except that a Watts solution was added in an amount that provided 100 ppm of nickel as a metal impurity. The trivalent chromium plating solution was subjected to the same test as in Example 1. The results are shown in Table 2.

Table 2

	Basic formulation	Compound	Addition concentration	L*	Evaluation of color tone	Evaluation of appearance	Throwing power decreasing rate (%)	Note
Example product	1	Na vinylsulfonate 25% aqueous solution	1 mL/L	78.97	good	good	4.93	-
	1	Na vinylsulfonate 25% aqueous solution	5 mL/L	79.83	good	good	4.23	-
	1	Na allylsulfonate 36% aqueous solution	0.5 mL/L	78.04	good	good	1.41	-
	1	Na p-styrenesulfonate	1.5 g/L	79.01	good	good	3.52	-
	2	Na β-styrenesulfonate	1.0 g/L	79.22	good	good	2.82	-
	2	Na vinylsulfonate 25% aqueous solution	1 mL/L	78.99	good	good	4.23	-

(continued)

	Basic formulation	Compound	Addition concentration	L*	Evaluation of color tone	Evaluation of appearance	Throwing power decreasing rate (%)	Note
Comparative product	1	not added	-	77.81	poor	poor	6.34	brown stripe pattern
	1	Na 2-propine-1-sulfonate 20% aqueous solution	0.1 mL/L	*	poor	poor	-	mostly deposition failure
	1	thiodiglycolic acid	1.0 g/L	76.48	poor	good	7.75	-
	1	thiourea	30 mg/L	75.3	poor	good	11.27	-
	1	1-allyl-2-thiourea	50 mg/L	76.08	poor	good	4.23	-
	1	Na 3-mercapto-1-propanesulfonate	50 mg/L	77.54	poor	good	5.63	-
	1	Na 2-hydroxyethanesulfonate 20% aqueous solution	20 mL/L	78.53	poor	poor	7.75	-
	1	Na saccharate dihydrate	50 mg/L	73.67	poor	poor	9.86	brown stripe pattern
	2	not added	-	77.59	poor	poor	6.85	brown stripe pattern
	3	not added	-	*	*	*	50% or more	mostly deposition failure
	3	Na allylsulfonate 36% aqueous solution	1.5 mL/L	*	*	*	50% or more	mostly deposition
								failure
	3	Na vinylsulfonate 25% aqueous solution	1.0 mL/L	*	*	*	50% or more	mostly deposition failure
*: unmeasurable or unevaluable								

[0043] It was found that the plating capability of the trivalent chromium plating solution of the present invention (i.e., the example product), which was a chloride bath and contained the unsaturated sulfonic acid compound having the particular structure, was not influenced by 100 ppm of nickel contained as a metal impurity in the plating solution. It was also found that irrespective of the same trivalent chromium plating solution, the sulfuric acid bath (i.e., the comparative product having the basic formulation 3) had no resistance against metal impurities even though the unsaturated sulfonic acid compound having the particular structure was contained. It was further found that irrespective of the chloride bath, in the case where the particular structure was not used, the plating capability was influenced by 100 ppm of nickel contained as a metal impurity in the plating solution.

[0044] 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 0.3% by atom, as measured by the EDS elemental analysis.

Example 3

Chromium Plating in presence of Impurity

[0045] A trivalent chromium plating solution containing the compounds shown in the basic formulation 1 used in Example 1 and the Table 3 below, and a copper chloride aqueous solution in an amount that provided 20 ppm of copper as a metal impurity was prepared. The trivalent chromium plating solution was subjected to the same test as in Example 1. The results are shown in Table 3. For comparison, a trivalent chromium plating solution containing no unsaturated sulfonic acid compound having the particular structure was subjected to the same test. The results are also shown in Table 3.

Table 3

	Basic formulation	Compound	Addition concentration	L*	Evaluation of color tone	Evaluation of appearance	Throwing power decreasing rate (%)	Note
Example product	1	Na vinylsulfonate 25% aqueous solution	2 mL/L	79.39	good	good	0.47	-
Comparative product	1	not added	-	79.14	good	poor	2.82	white pattern

[0046] It was found that the plating capability of the trivalent chromium plating solution of the present invention (i.e., the example product) was not influenced by 20 ppm of copper contained as a metal impurity in the plating solution.

[0047] 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 0.3% by atom, as measured by the EDS elemental analysis.

Example 4

Chromium Plating

[0048] The compounds shown in the following basic formulation 4, a sodium vinylsulfonate 25% aqueous solution, and nickel (added in the form of nickel chloride) were dissolved in water in the concentrations shown in Table 4 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 5 A and a plating time of 3 minutes. The trivalent chromium plating solution was subjected to the same test as in Example 1. The presence of burnt deposit in a high current density (which was the left end portion in Fig. 1) was visually evaluated. The results are shown in Table 4. For showing an example of the presence of burnt deposit, the brass plate after plating with a plating solution containing no nickel (with burnt deposit) is shown in Fig. 2, and the appearance of the brass plate after plating with a plating solution containing 10 ppm of nickel (without burnt deposit) is shown in Fig. 3.

<Basic Formulation 4>

Basic chromium sulfate	64 g/L
Ammonium formate	16 g/L
Sodium chloride	70 g/L
Potassium chloride	140 g/L
Ammonium chloride	85 g/L
Ammonium bromide	6 g/L
Boric acid	67 g/L

Table 4

	Basic formulation	Na vinylsulfonate 25% aqueous solution	Nickel	L*	Evaluation of color tone	Evaluation of appearance	Burnt deposit in high current density
Example product	4	3 mL/L	10 ppm	79.57	good	good	none
	4	3 mL/L	30 ppm	80.42	good	good	none
	4	3 mL/L	50 ppm	80.28	good	good	none
	4	5 mL/L	300 ppm	79.91	good	good	none
	4	5 mL/L	500 ppm	79.57	good	good	none
Comparative product	4	3 mL/L	0 ppm	80.27	good	good	found

[0049] It was found that burnt deposit in a high current density in plating was prevented from occurring, by positively using nickel as a metal impurity contained in the trivalent chromium plating solution of the present invention (i.e., the example product).

[0050] 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

0.3% by atom, as measured by the EDS elemental analysis.

Reference Example 1

Chromium Plating

[0051] To a plating solution having the basic formulation 4, a sodium vinylsulfonate 25% aqueous solution was not added, but nickel was added in an amount of 0, 10, 30, or 50 ppm, so as 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 5 A and a plating time of 3 minutes. The trivalent chromium plating solution was subjected to the same test as in Example 1 and the same evaluation of the presence of burnt deposit in a high current density as in Example 4.

[0052] It was found that by positively using nickel as a metal impurity contained in the trivalent chromium plating solution of the present invention, the color tone and the appearance of the resulting plating were equivalent to the case where plating was formed with the solutions having a sodium vinylsulfonate 25% aqueous solution added thereto in Examples 1 to 3, and burnt deposit in a high current density in plating was prevented from occurring. In the case where nickel was not added, burnt deposit in a high current density in plating occurred.

Industrial Applicability

[0053] 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 chloride as a conductive salt, a pH buffering agent, and a complexing agent,
   further comprising an unsaturated sulfonic acid compound represented by the following general formula (1):

   $$R_1\text{-CH=CH-}R_2\text{-SO}_3X \qquad (1)$$

   wherein in the formula (1), R_1 represents a hydrocarbon group having a number of carbon atoms of from 1 to 10, hydrogen, or a halogen; R_2 represents nothing or a hydrocarbon group having a number of carbon atoms of from 1 to 10; and X represents hydrogen or an alkali metal.

2. The trivalent chromium plating solution according to claim 1, wherein the unsaturated sulfonic acid compound is one kind or two or more kinds selected from the group consisting of sodium vinylsulfonate, sodium allylsulfonate, sodium p-styrenesulfonate, and sodium β-styrenesulfonate.

3. The trivalent chromium plating solution according to claim 1, wherein the chloride is one kind or two or more kinds selected from the group consisting of potassium chloride, ammonium chloride, and sodium chloride.

4. The trivalent chromium plating solution according to any one of claims 1 to 3, wherein the trivalent chromium plating solution further comprises a metal impurity.

5. The trivalent chromium plating solution according to any one of claims 1 to 4, wherein the trivalent chromium plating solution further comprises nickel.

6. The trivalent chromium plating solution according to any one of claims 1 to 5, wherein the trivalent chromium plating solution comprises substantially no iron and/or cobalt.

7. A trivalent chromium plating method comprising electroplating an article to be plated with the trivalent chromium plating solution according to any one of claims 1 to 6.

8. A method for enhancing resistance of a trivalent chromium plating solution containing a trivalent chromium compound, a chloride as a conductive salt, a pH buffering agent, and a complexing agent, against metal impurities contained, comprising using an unsaturated sulfonic acid compound represented by the following general formula (1):

$$R_1\text{-CH=CH-}R_2\text{-SO}_3X \qquad (1)$$

wherein in the formula (1), R_1 represents a hydrocarbon group having a number of carbon atoms of from 1 to 10, hydrogen, or a halogen; R_2 represents nothing or a hydrocarbon group having a number of carbon atoms of from 1 to 10; and X represents hydrogen or an alkali metal, further contained in the trivalent chromium plating solution.

9. A method for preventing burnt deposit in a high current density in plating with a trivalent chromium plating solution containing a trivalent chromium compound, a chloride as a conductive salt, a pH buffering agent, and a complexing agent, comprising using an unsaturated sulfonic acid compound represented by the following general formula (1), and nickel:

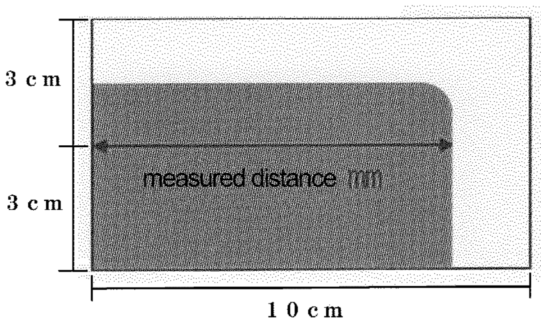
$$R_1\text{-CH=CH-}R_2\text{-SO}_3X \qquad (1)$$

wherein in the formula (1), R_1 represents a hydrocarbon group having a number of carbon atoms of from 1 to 10, hydrogen, or a halogen; R_2 represents nothing or a hydrocarbon group having a number of carbon atoms of from 1 to 10; and X represents hydrogen or an alkali metal, further contained in the trivalent chromium plating solution.

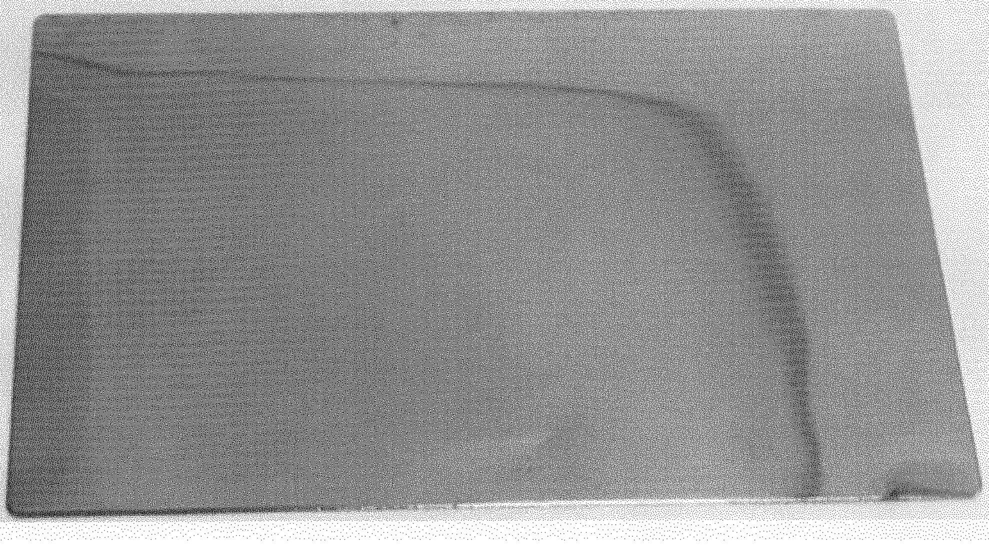
10. A chromium-plated product comprising an article to be plated, electroplated with the trivalent chromium plating solution according to any one of claims 1 to 6.

11. The chromium-plated product according to claim 10, wherein the chromium plating contains substantially no iron and/or cobalt.

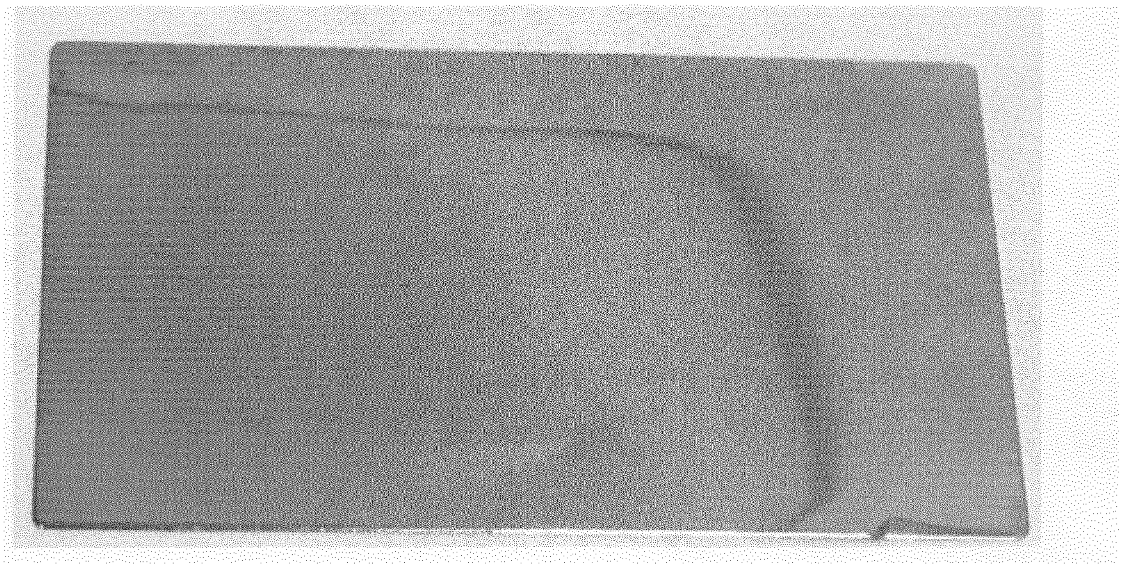
[FIG.1]



[FIG.2]



[FIG.3]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/045799

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2016-172933 A (ATOTECH DEUTSCHLAND GMBH) 29 September 2016, example 8 & US 2014/0042033 A1 example 8 & WO 2012/150198 A2 & EP 2886683 A2 & TW 201250065 A & CA 2834109 A & KR 10-2014-0027200 A & ES 2578503 T & PL 2705176 T	1-11
A	JP 57-152483 A (W. CANNING MATERIALS LIMITED) 20 September 1982, claims, page 3, lower right column, line 12 to page 6, lower right column, line 16, example 9 & US 4473448 A claims, column 2, line 15 to column 6, line 29, example 8 & 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.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search 04 February 2019 (04.02.2019)	Date of mailing of the international search report 12 February 2019 (12.02.2019)
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

Patent documents cited in the description

- JP 2009074170 A **[0005]**